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„Graphene Coating Generation by the
Electrochemical and
Femtosecond Laser-Assisted
Reduction of Graphene Oxide“

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"I am not young enough to know everything."

- Oscar Wilde

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Abstract

Faculty of Chemistry

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Graphene Coating Generation by the Electrochemical and Femtosecond Laser-Assisted Reduction of Graphene Oxide

by Martin Pfaffeneder-Kmen, BSc MSc

Graphene Oxide is a two-dimensional material, consisting of sp_2 -hybridized carbon, sp_3 -hybridized carbon, and a certain amount of oxygen-containing groups. It can be obtained from graphite oxide by exfoliation. Due to the non-planar structure, which results in a higher spacing between the sheets in graphite oxide, the attractive forces between the sheets are weaker as compared to graphite. Furthermore, the oxygen-containing groups cause hydrophilicity and solubility in water.

This and other properties make graphene oxide an interesting object of study. This work investigated the reduction of graphene oxide. Its reduction leads to reduced graphene oxide which exhibits a graphene-like structure. Therefore, it is proposed as a precursor material for many applications, which require a low-cost and easy to perform synthesis of graphene. The higher amount of defects excludes it from some applications, which were proposed for graphene, but also opens other fields.

Two approaches are shown in this work: the one-step-approach and the two-step-approach. In the one-step-approach, the coating and reduction of graphene oxide occur concurrently directly out of the graphene oxide suspension. An electrochemical quartz crystal microbalance was utilized to perform mass-sensitive measurements during the electrochemical deposition of graphene oxide. Platinum coated quartzes served as working electrodes. Cathodic and anodic polarization resulted in the deposition by dissimilar mechanisms, which are electrochemical reduction and specific adsorption, respectively.

The two-step approach separates the coating and the reduction step. A reproducible coating procedure was developed. Graphene oxide coatings were deposited by spin-coating. Grooves down to the substrate were ablated by fs-laser treatment in order to determine the

coating thicknesses by a scanning force microscope.

Moreover, the fs-laser-assisted reduction of graphene oxide coatings as an alternative to the electrochemical approach was demonstrated. The resulting reduced graphene oxide was characterized by Raman-spectroscopy and scanning electrochemical microscopy.

Finally, a scanning electrochemical microscope served to reduce graphene oxide coatings. A microelectrode was positioned on a graphene oxide coating. A cathodic polarization triggered the lateral growth of a reduced graphene oxide disk. The characterization was performed by Raman-spectroscopy and optical microscopy.

The mechanism of the electrochemical reduction was investigated by *in-situ* attenuated total reflection FTIR spectroscopy. A multivariate method was applied for evaluating the spectra. It could be shown that the reduction occurs in two steps. At first graphene oxide is reduced to α -reduced graphene oxide. In a second step, it is reduced to β -reduced graphene oxide.

Zusammenfassung

Fakultät für Chemie

Institut für physikalische Chemie

Die Erzeugung von Graphenbeschichtung durch die Elektrochemische und Femtosekunden-Laser-Pulse Unterstützte Reduktion von Graphenoxid

von Martin Pfaffeneder-Kmen, BSc MSc

Graphenoxid ist ein zweidimensionales Material, bestehend aus sp_2 -hybridisiertem Kohlenstoff, sp_3 -hybridisiertem Kohlenstoff und einer gewissen Menge sauerstofffunktioneller Gruppen. Es kann aus der Exfoliation von Graphitoxid hergestellt werden. Aufgrund der nicht-planaren Struktur, die zu einem größeren Abstand zwischen den Schichten in Graphitoxid führt, sind die Anziehungskräfte zwischen diesen schwächer im Vergleich zu Graphit. Darüber hinaus bewirken die sauerstoffhaltigen Gruppen Hydrophilie und somit Löslichkeit in Wasser. Diese und andere Eigenschaften machen Graphenoxid zu einem interessanten Studienobjekt. Die vorliegende Arbeit untersuchte die Reduktion von Graphenoxid. Dessen Reduktion führt zu reduziertem Graphenoxid, welches eine graphenartige Struktur aufweist. Daher wird es als Vorstufe für viele Anwendungen, die eine kostengünstige und einfach durchzuführende Synthese von Graphen erfordern, vorgeschlagen. Die höhere Anzahl an Defekten schließt es von einigen Anwendungen aus, welche für Graphen vorgeschlagen wurden. Aber auch andere Gebiete werden dadurch erschlossen.

In dieser Arbeit werden zwei Ansätze gezeigt: der einstufige und der zweistufige Ansatz. Im einstufigen Ansatz erfolgt die Beschichtung und Reduktion von Graphenoxid gleichzeitig direkt aus der Graphenoxid-Suspension. Eine Elektrochemische Quarz-Mikrowaage wurde verwendet, um massensensitive Messungen während der elektrochemischen Abscheidung durchzuführen. Als Arbeitselektroden dienten platinbeschichtete Quarze. Die kathodische und anodische Polarisierung führte zu einer Abscheidung durch unterschiedliche Mechanismen, einerseits die elektrochemische Reduktion und andererseits die spezifische Adsorption.

Der zweistufige Ansatz trennt den Beschichtungs- und den Reduktionsschritt. Ein reproduzierbares Beschichtungsverfahren wurde entwickelt. Graphenoxidschichten wurden mittels Spin-Coating abgeschieden. Rillen bis zum Substrat wurden mittels fs-Laser-Behandlung abgetragen, um die Schichtdicken mit einem Rasterkraftmikroskop zu bestimmen.

Darüber hinaus ist die fs-Laser-unterstützte Reduktion von Graphenoxidschichten als Alternative zum elektrochemischen Ansatz demonstriert worden. Das daraus resultierende reduzierte Graphenoxid wurde durch Raman-Spektroskopie und elektrochemische Rastermikroskopie charakterisiert.

Schließlich diente ein elektrochemisches Rastermikroskop dazu, Graphenoxidschichten zu reduzieren. Eine Mikroelektrode wurde auf einer Graphenoxidschicht positioniert. Eine kathodische Polarisierung löste das laterale Wachstum einer reduzierten Graphenoxidscheibe aus. Die Charakterisierung wurde durch Raman-Spektroskopie und optische Mikroskopie durchgeführt.

Der Mechanismus der elektrochemischen Reduktion wurde mit Hilfe der in-situ ATR-FTIR-Spektroskopie untersucht. Zur Auswertung der Spektren wurde eine multivariate Methode angewandt. Es konnte gezeigt werden, dass die Reduktion in zwei Schritten erfolgt. Zuerst wird Graphenoxid zu alpha-reduziertem Graphenoxid reduziert. In einem zweiten Schritt wird es zu beta-reduziertem Graphenoxid reduziert.

Preface

This thesis arose between November 2014 and January 2018. My Master thesis "Graphene-based coatings on metal electrodes" from 2014 was dedicated to the same topic. Some of its results were incorporated in chapter 2.

Two publications were published during the work for this thesis. *In Situ FTIR and in Situ QMB Study of the Electrochemistry of Graphene Oxide on Platinum* [84] covers basically the results of chapter 2. The results of chapters 3 and 6 were published in *In Situ FTIR and in Situ QMB Study of the Electrochemistry of Graphene Oxide on Platinum* [83]. Both publications are appended to the work. On some positions in the text it is referred to them.

The thesis is structured in seven chapters. Chapter 1 contains a general introduction to the materials graphene, graphene oxide, and reduced graphene oxide. This thesis concerns exclusively graphene oxide and reduced graphene oxide. They cover a peripheral topic with other techniques and instruments than the mainstream topic graphene.

Chapters 2 to 6 present the results of this work, whereby each chapter is introduced and concluded individually. Chapter 7 concludes and summarizes the whole thesis.

Martin Pfaffeneder-Kmen

Vienna, 2018

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Abbreviations

AFM	A tomic F orce M icroscopy
CE	C ounter E lectrode
CV	C yclic V oltammetry
CVD	C hemical V apour D eposition
DMF	D imethyl f ormamide
CVD	E lectro p horetic D eposition
EQCM	E lectrochemical Q uartz C rystal M icrobalance
GO	G raphene O xide
IR	I nfra R ed
IUPAC	I nternational U nion of P ure and A ppplied C hemistry
LSV	L inear S weep V oltammetry
NMP	N - M ethyl-2- P yrrolidone
O	O xidized form of a redoxactive species
PAC	P robe A pproach C urve
PBS	P hosphate B uffer S olution
R	R educed form of a redoxactive species
RE	R eference E lectrode
rGO	r educed G raphene O xide
SECM	S canning E lectrochemical M icroscope
UME	U ltramicroelectrode
WE	W orking E lectrode

Symbols

A	Surface Area	(cm^2)
c	Concentration	$(\frac{mol}{dm^3})$
E	Potential	(V)
f	Frequency	(Hz)
f_0	Resonance Frequency	(Hz)
i	Current Density	$(\frac{A}{cm^2})$
i_0	Current Density far Away From the Substrate Electrode	$(\frac{A}{cm^2})$
m	Mass	(g)
M	Molar Mass	$(\frac{g}{mol})$
n	Number of Involved Electrons	$(\frac{1}{mol})$
T	Temperature	(K)
z	Formal Charge of an Ion	(e)
μ	Shear Modulus	$\frac{g}{cm \cdot s^2}$

To my family

Chapter 1

Introduction - Graphene and Graphene Oxide

The justification of the Nobelprize Committee 2010 for awarding the Nobelprize for Physics to Andre Geim and Konstantin Novoselov was:

"for groundbreaking experiments regarding the two-dimensional material graphene" [78]

"Groundbreaking" is very accurate to describe the scientific achievements, which were honoured in this context. Unlike many people think, the prize was not awarded for the discovery of graphene. Actually graphene was already known since decades - at least in theory [3]. Geim and Novoselov opened a new chapter in the scientific society. They catalysed research in many different areas all over the world and turned graphene from a theoretical curiosity to one of the main stream research topics. In the past few years countless publications were published on this topic, books were written, conferences were organized and much more - just on the topic graphene.

The interest of people widened to other two-dimensional materials, like graphene oxide (GO), reduced graphene oxide (rGO), MoS_2 or hexagonal boronnitride [77]. This work focuses on GO and rGO. Initially GO and rGO were investigated to solve the problem of graphene production. Today, the specific properties of these materials - which are unlike the ones of graphene - are used for various ideas and applications on their own.

Nevertheless, since graphene is the historic ancestor of all two-dimensional materials, it makes sense to report on it, before coming to GO and rGO.

1.1 Graphene

Carbon and its allotropes always fascinated scientist all over the world. Graphene - a single honeycomb lattice layer of carbon atoms - was understood as the building block of graphite. Not only graphite, but all graphitic allotropes, can be build out of graphene. Therefore one can call graphene as *"mother of all graphitic forms"* [39], compare Fig. 1.1.

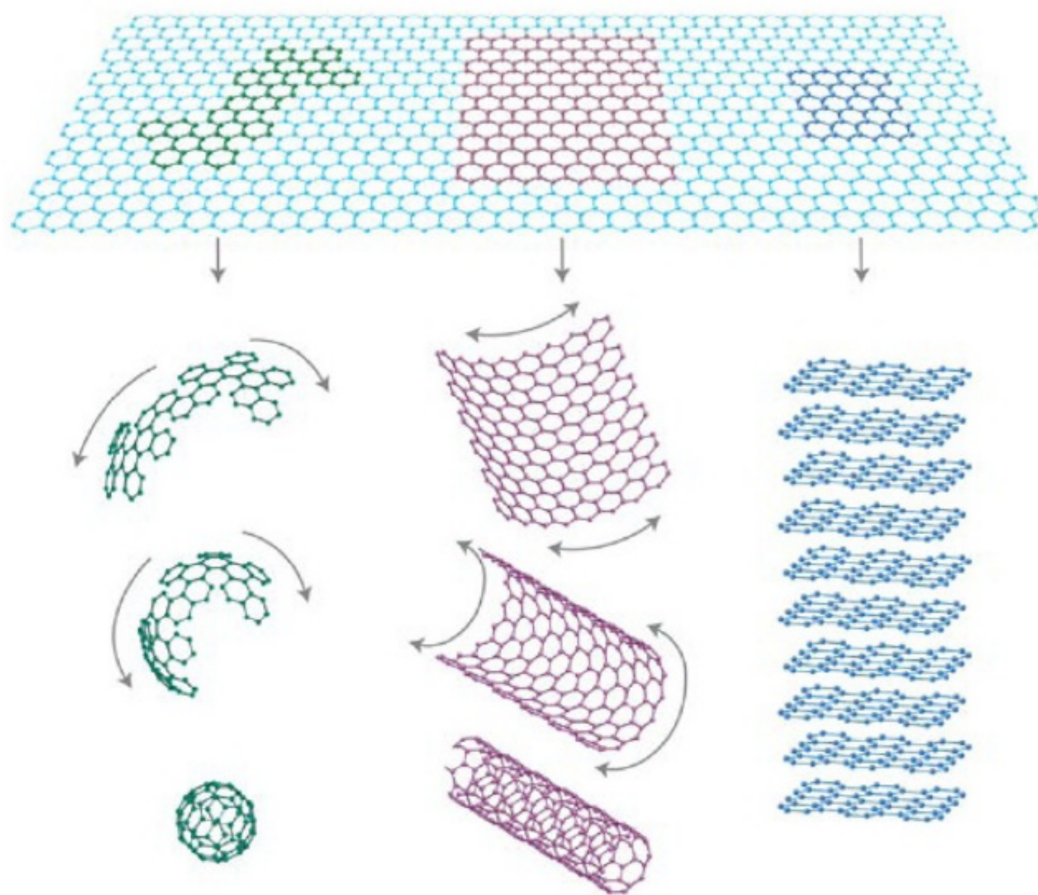


Figure 1.1: Graphene as the mother of carbon allotropes. It can be rolled up to fullerene, nanotubes, or stapled to graphite. Reproduced with permission [39].

The first reports about graphene were of theoretical nature and date back to the middle of the last century [104]. Afterwards a discussion about the stability of graphene followed. Supported by theoretical works and also experiments, people thought that any two-dimensional crystals cannot be thermodynamically stable [39].

It was the famous publication of the two Nobel prize laureates - Andre Geim and Konstantin Novoselov - which taught us better [79]. Since then the door was opened to research on this material and many important papers were published, ranging from basic research to sophisticated applications.

1.1.1 Structure and Properties of Graphene

The remarkable properties of graphene are due to its structure. Graphene is more than just thin graphite. A simple demonstration shall confirm this: when comparing one perfect

one-atom-thick graphene layer with a graphite crystal, this becomes obvious. Graphene has a 6-fold rotation axis, orthogonal to the plane [81]. In graphite every second layer is shifted, which results in a 3-fold rotation axis perpendicular to the planes. Just this little detail shows that graphene and graphite have different symmetries and thus different properties. Therefore, graphene is more than just thin graphite. It must be regarded as an autonomous material.

But where is the border between graphite and graphene? Strictly spoken, only one atom thick layers would be graphene. This is also the description of the IUPAC [49]:

"A single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size."

However, scientists observed that also few-layer graphene has exceptional properties. The properties become more and more graphitic, when reaching ten layers or more [39].

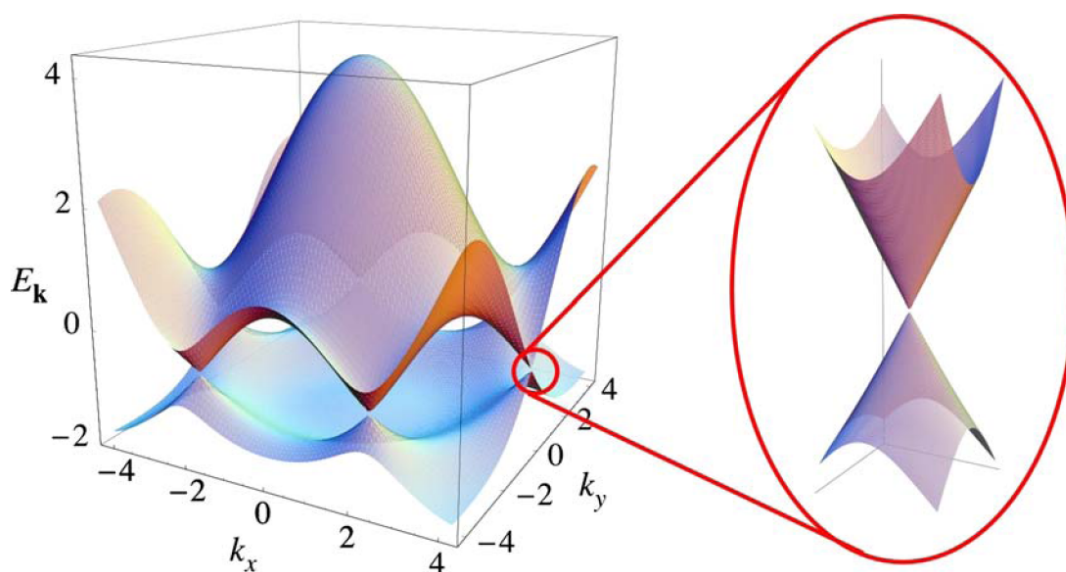


Figure 1.2: Band structure of graphene. Reproduced with permission [18].

The band structure of graphene is remarkable, which is shown in Fig.1.2. The unique point in this structure is that valence and conduction band touch at one point [2, 18]. They do neither overlap, nor build a band gap. Therefore, graphene can be classified between conductors and semi-conductors. This property was entitled as "Zero-Band-Gap". [39]

High quality graphene exhibits an extremely high charge carrier mobility. It can be reported to be higher than $15000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and may rise under perfect conditions even up to $100000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [2, 39].

Graphene is a chemically very inert material. However, it is often of interest to functionalize

graphene. There are basically two strategies to do so. The *covalent functionalization* bases on breaking sp^2 bonds, whereas the *non-covalent functionalization* does not. Here, $\pi - \pi$ stacking is often the binding force. [2]

Besides electronic and mechanical properties, the mechanical properties of graphene gained many researchers' interests. By utilising an AFM tip, the mechanical properties of a single free standing graphene sheet can be measured. The measurements delivered a Young Modulus of appr. 1 TPa, which results in an Elastic Stiffness of 355 Nm^{-2} . Thus, graphene is the strongest material ever measured. [2]

1.1.2 Preparation of Graphene

Generally there are two approaches for preparing graphene: the Top-Down and the Bottom-Up approach. The Top Down methods basically try to separate graphite into its single sheets, whereas Bottom-up methods build graphene out of smaller units (f.i. molecules) [4].

Novoselov and Geim [79] followed in their work the Top-Down strategy. By mechanical exfoliation - also known as "*Scotch Tape*® *Method*" - they kind of peeled the single layers off with an adhesive tape and deposited them on a substrate.

This method exhibited to be useful in research, because it needs simple facilities and the quality of the thus obtained graphene is very good. However, single layered graphene sheets must be searched on a silicon wafer, the yield is low and the implementation to any industrial process is conceivably poor. So, there was soon the demand for easier processable synthesis methods.

Other Top-Down approaches are the liquid exfoliation of graphite [77], the electrochemical exfoliation [71], or the reduction of graphene oxide [82]. We will report on the latter later.

The most common synthesis method in the graphene world is chemical vapour deposition (CVD) [112]. A H_2/CH_4 mixture is flown over a Cu or Ni foil, where it degenerates and builds graphene. Afterwards the metal foil can be etched away to transfer graphene to another substrate. Although, the quality of CVD graphene is very high, it must be mentioned in this context that CVD-graphene is always polycrystalline [99].

Other Bottom-up methods would be the epitaxial growth on SiC or the chemical synthesis, where graphene is treated as polycyclic aromatic hydrocarbon [4]. By epitaxial growth wafer-sized graphene was already grown. Therefore it is also a promising candidate for industrial

applications. Chemical synthesis managed until now only to produce only very small flakes of graphene.

1.1.3 The Electrochemistry of Graphene

The electrochemistry of graphene is not as rich and sophisticated as the one of GO [5]. Nevertheless, it is worth mentioning in this context, because it affects the properties of rGO. In this context graphene is often compared to graphite. Therefore the electrochemistry of graphene tells us also a lot about the electrochemistry of graphite. Here the question arises, whether the concepts may not always be totally applicable vice-versa. Velický [101] showed 2014 that at least the heterogeneous electron transfer rate does not depend on the number of graphene layers.

It is supposed that the electron transfer takes place at the edges of graphene or at defects. This is one reason, why GO and rGO are electrochemically more active - due to the higher defect density. Nonetheless, recent studies showed that the basal planes may also play an important role in graphene electrochemistry [63, 101].

1.1.4 Possible Applications

The applications of graphene are versatile. The main areas of applications may be divided in sensing and energy systems. Thus, the applications of graphene were proposed in electroanalysis, supercapacitors, and graphene based batteries. [4, 16].

Graphene shows a high conductivity and is more or less transparent. Therefore it is suitable for transparent electrodes, which are necessary for photovoltaic cells [112]. At the moment the state of the art technique is the use of indium tin oxide (ITO), because of its high conductivity and optical transparency. However, the availability of Indium may become a problem. Graphene technology could substitute ITO and solve this issue. Graphene is a promising candidate for replacing ITO in all aspects for thin film devices, such as solar cells, light organic light emitting diodes, or touchscreens [107].

1.2 Graphene Oxide and Reduced Graphene Oxide

The first description of GO dates back more than one and a half centuries [15]. At that time it was entitled as graphitic acid, a product obtained by the treatment of graphite with strong oxidative agents. As described above, the hype of graphene has raised the demand for new synthesis methods of graphene, where the reduction of GO was one possibility [30, 32]. The reduction process must still be optimized, since rGO exhibits many structural defects [82]. However, the renaissance of GO was catalysed through this research. Today, a few years later, GO is not only a possible precursor for graphene, but many applications of the material itself and its derivatives were proposed [20, 82].

1.2.1 Structure and Properties of Graphene Oxide

The structure of graphene oxide is since its first preparation under heavy discussion [32]. Since GO is produced by the oxidation of graphite, it was assumed, that it consists of carbon and oxygen atoms - in a layered structure. The earliest interpretations are stoichiometric and ordered. Later the idea of a non-stoichiometric, non-ordered structure was born.

Hofmann and Holst [46] proposed 1939 a structure regarding epoxide functions as oxygen containing group. They had the idea of the stoichiometric relation C_2O . Ruess [87] introduced 1947 alcohol groups to the model of Hofmann. He also published that the C:O ratio is not strict, but within certain borders. A heavy discussion followed. Clauss [25] proposed a structure with even more oxygen containing groups. The structure was discussed [90] by Scholz 1969. Mermoux [73] introduced 1991 again a molecular formula: $C_8O_2(OH)_2$. Nakajima and Matsuo [75, 76] had even the idea of a scaffold-type structure. Finally Lerf and Klinowski [65] published their famous model 1998.

The Lerf-Klinowski model suggests a graphene sheet, decorated randomly with epoxide and alcohol groups at the basal planes and carboxylic acid groups at the edges (Fig. 1.3). The carbon atoms, binding to oxygen are now sp_3 -hybridized. Therefore the sheet is not flat anymore, but wrinkled. The interlayer distance also increases, which can be seen in XRD [98] or AFM [43] measurements, it raises to 0.8 – 1.1 nm. For comparison: graphite has an interlayer distance of 0.335 nm [43].

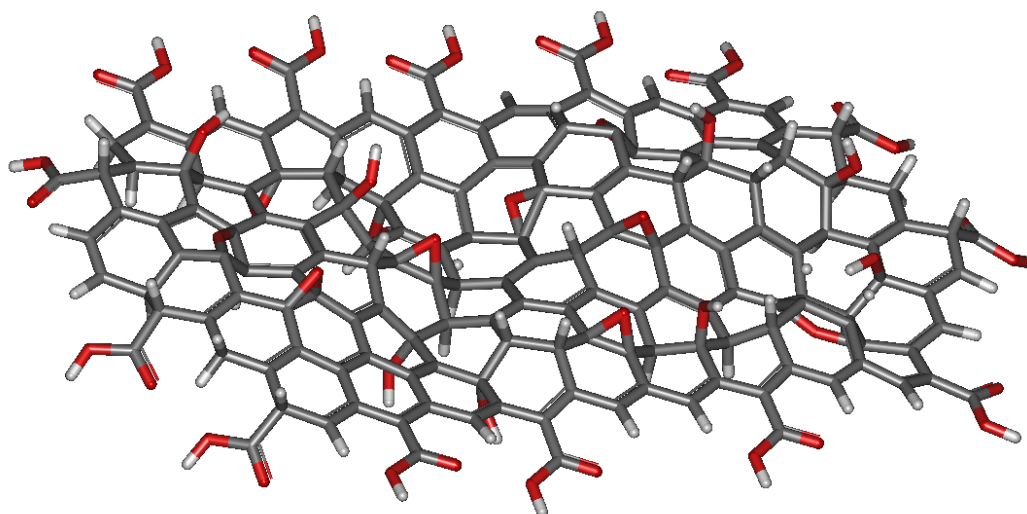


Figure 1.3: Molecular structure of graphene oxide.

The oxidation also affects its behaviour in water. GO can be dispersed into single sheets in water. This effect works especially at elevated pH ($\text{pH} > 3.5$). Then, the carboxylic acid groups are dissociated and GO exhibits a negative Zeta potential of -35 mV. At lower pH (about pH2) these carboxylic acid groups are protonated, which results in a less negative Zeta potential of -15 mV. GO tends to agglomerate [44].

A comparison with other solvents shows, that GO tends to disperse better in polar solvents, like water, acetone or ethanol. In water, DMF or NMP GO suspensions are even stable for weeks [80].

1.2.2 Structure and Properties of Reduced Graphene Oxide

The easiest way for following the reduction of GO to rGO is by observing the colour. GO is greenish to brownish or yellow - depending on the degree of oxidation. The reduction process changes GO to the black rGO, which has usually a metallic glimmer. [82]

One of the most important characteristics of rGO is the conductivity. GO is an insulator because of the sp_3 hybridization of a part of the carbon atoms. The sp_2 conjugated lattice gets partially restored during the reduction process. Thus, rGO is a conductor with a conductivity of 350 S/cm (measured at a single sheet). [82]

Of course these characteristics strongly depend on the structure. One observable for this is the C:O ratio, which is usually measured by XPS [98]. The C:O ratio of GO ranges usually between 2 and 4. After the reduction it is around 10, depending on the reduction technique

[82]. From these numbers it can be seen, that the reduction of GO is by far not complete. At least as important as the C:O ratio is the structure of the lattice. In contrast to pristine graphene, rGO contains a considerable proportion of defects. This affects its properties, especially the conductivity due to presence of pentagons, heptagons and other structural defects which prohibit π -conjugation [42].

1.2.3 Reduction Methods of Graphene Oxide

Electrochemical Reduction. This thesis focuses mainly on the electrochemical reduction of GO. The process is straight forward. GO has to be somehow in direct contact with the working electrode. This can be either realized by coating the working electrode with GO [43] or rGO serves itself as working electrode [114]. The electrode is then polarized cathodically [82] to remove oxygen containing groups. This method is classified as environmentally benign, because - in contrast to the chemical reduction - no organic solvents or strong reducing agents are necessary [43].

Photo Reduction. The photoreduction of GO with a xenon lamp bases basically on thermal energy [82], which induces the reduction of oxygen containing groups. A more sophisticated method was published by Zhang et al. in 2010 [111, 113]. They used a femtosecond laser to reduce graphene oxide. This has the benefit that any pattern can be reduced in GO.

Chemical Reduction. The use of chemical reductants is probably the most common method of reducing GO. The main benefit is the easy processing. Colloidal GO and GO films can be treated with solutions containing the reducing agent. Hydrazine was the first reagent ever used for this procedure. This, its derivatives and metal hydrides like sodium borohydride are widely used reductants for GO [82].

Thermal Reduction. Thermal annealing leads to the reduction of GO. The first attempts for producing graphene out of GO worked through rapid thermal annealing with more than 2000 °C/min. The sudden generation of CO and CO₂ resulted in the exfoliation of graphite oxide [82]. Under specific conditions and introducing methane as carbon source, the thermal

reduction leads to improved recovery of the graphene lattice and therefore to high-quality graphene [28].

Microwave Reduction. The microwave reduction is a special form of the thermal reduction. It is preferable, because it works more rapidly and homogeneous [82].

Photocatalyst Reduction. TiO_2 nanoparticles were used as photocatalytic nanoparticles for the reduction of GO. A suspension of GO and TiO_2 nanoparticles was irradiated with UV-radiation. The mechanism was proposed to work on a charge separation on the nanoparticle surface and the involvement of ethanol as solvent [82].

Solvothermal Reduction. In the solvothermal reduction GO and a solvent are heated in a sealed compartment. It can be heated above the boiling temperature and even above its supercritical point. As solvents water or organic solvents can be used. It was shown that this process can recover the conjugated lattice of graphene [82].

Multistep Reduction. To improve the results of the reduction of graphene oxide, routines were introduced to reduce GO in more than a single step. The above described methods - especially the thermal and chemical reduction - were combined to improve the characteristics of rGO. The conductivity served as observable for a successful, high-quality reduction [82].

1.2.4 Reduction mechanism

The reduction mechanism of GO is an open question. Since the structure of GO is still under discussion [32] and the synthesis and reduction parameters affect its characteristics strongly [36], this question must be drawn up for a certain system, i.e. one defined reduction method for one defined GO. In this work, this will be the electrochemical reduction of GO, synthesized by modified Hummers' method [108]. However, people elaborated some mechanistic details for the GO reduction, which shall be reviewed in this context.

The most obvious question is the elimination of oxygen-containing groups. Ex-situ characterizations, i.e. before and after the reduction procedure, show a picture of the final product

- rGO - in comparison to the initial GO. Zhou [115] did this for the chemical reduction with hydrazine and the hydrothermal reduction. Guo [43] followed a similar approach for the electrochemical reduction of GO. Techniques like molecular spectroscopy or XPS could identify the reduction of oxygen-containing functionalities, like f.i. O–H groups.

The *ex-situ* approach is important, because it characterizes the final product. Though, it lacks the ability to describe the mechanism of the reduction. A deeper understanding of the process will help to control the process better. Thus, *in-situ* methods are necessary for the characterization of the material *during* the reduction process.

Viinikanoja [102, 103] investigated the electrochemical reduction of GO in water and organic solvents. The degeneration of oxygen-containing groups could be followed. However, some question remained open. Especially the potential dependent progression of the reduction of these groups stayed unexplained.

The next important step is the healing of defects and the regeneration of a conjugated lattice [82]. The generation of a conjugated lattice is the prerequisite for electrical conductivity. Structural defects like pentagons, heptagons, or missing carbon atoms impair the electrical properties of rGO in comparison to perfect graphene. Healing these defects would pave the way to produce high-quality graphene out of GO. Dai showed 2011 [28] that the healing of defects in GO is in principle possible.

1.2.5 The Electrochemistry of Graphene Oxide

Due to the complex structure of GO, which was described in Section 1.2.1, its electrochemistry is diverse. Gaining a deeper understanding is challenging, because the exact molecular structure is still under discussion. It is therefore difficult to assign certain reduction or oxidation potentials.

Anyhow, people tried to describe the electrochemistry of GO. A straight forward approach was its characterization by measuring cyclic voltammetries of immobilized GO coatings [36]. It was found, that depending on the synthesis method of GO, the CVs looked completely different. Conclusively, the synthesis has a non-negligible impact on the structure and therefore on the properties of GO.

The CVs of four different GOs were investigated: synthesized by Staudenmaier, Hofmann,

Hummers and Tours method. They can be roughly divided into two groups. In Staudenmaier's and Hofmann's GO chlorate is the oxidant for the synthesis; in Hummers' and Tour's it is permanganate. All GOs can be reduced cathodically, but only the ones synthesized with permanganate can be oxidized subsequently. Permanganate GOs show in general a more complex CV, which depends on the CV cycle and consists of several composed cathodic and anodic waves.

The electrochemical reduction of graphene oxide is stated as green alternative [43] to the chemical reduction, where environmentally critical chemicals like hydrazine must be used. The properties of the starting material are as important for the quality final product as the electrochemical parameters. An incompletely oxidized GO could lead to better results [32]. Generally, it can be stated that the production of graphene like coatings via the electrochemical reduction of GO is a promising route for the future, but not mature yet. A deeper understanding of the electrochemistry of GO and its mechanism could lead to better controllability of the process.

1.2.6 Applications of Graphene Oxide and Reduced Graphene Oxide

The unique properties of GO make this material interesting in many fields of applications. Here, some ideas of possible applications shall be presented. However, the list of the referenced pioneering publications is by far not complete. But it shows the importance of gaining better understanding of this material.

The most obvious application is as precursor to graphene [41], which enables at least in theory all proposed publications for graphene. A few were discussed in section 1.1.4. The problem of this concept is that many applications proposed for graphene require a certain quality of the material, especially its electronic properties underlie stringent requirements. Therefore, either the quality of rGO must comply the demands of the application or the quality of final product must be further improved, like described in section 1.2.1.

GO is often proposed in sensoric applications. Especially in the field of biology, like f.i. enzyme biosensors, immunosensors, or DNA-sensors, all on the the basis of electrochemistry [22], GO is a promising material. But also as humidity sensor [14], incorporated in mobile phones, it can be used. These sensors have GO as sensitive surface for impedance spectroscopy measurements. GO was also immobilized on a QCM for humidity sensing [109]. A

prototype for TNT sensing on electrochemical basis was build with GO as precursor material [96].

Chapter 2

Graphene Oxide Reduction and Coating - One-Step-Approach

2.1 Introduction

For the production of rGO coatings basically two routes can be followed: the one-step-approach and the two-step-approach [98]. The two-step approach follows the idea that suspended exfoliated GO shall be coated onto a substrate in a first step and in a second step it is reduced or modified. All other chapters will be based on this strategy. Here, in this chapter, the one-step-approach will be discussed.

One-step-approach means the simultaneous deposition and reduction of GO. The benefit is that the procedure misses an extra reduction step. Therefore it can be faster and easier to perform than the two-step approach. However, the controllability of the reduction and deposition parameters is more difficult.

The mechanism of this process is not completely understood. It was shown [23] that the deposition of an rGO film on glassy carbon electrodes enhances its electrochemical signal. This may be because of its conductivity, the increased surface area and structural defects. The same group [23] supposed that the reduction and deposition mechanism may be an initial electrochemical reduction of GO and a consequent decrease of its dispersability in water. Therefore it will be immobilized on the electrode surface.

Many synthesis approaches for applications base on this approach [19, 23, 54, 67, 85]. A better understanding of the mechanism would pave the way for an easier and improved implementation of such ideas.

2.2 Electrochemical Quartz Crystal Microbalance (EQCM)

An EQCM is an instrument, which allows to follow mass changes during an electrochemical experiment [11]. It is easy to perform and many metals are available as electrode materials. The interpretation of the results is sometimes challenging, because not solely mass changes affect the observed signal.

The principle of these technique relies on the piezoelectric effect [17]. An electric potential causes a mechanical deformation of a piezoelectric material. An alternating potential causes a periodic vibration of the piezoelectric crystal.

Usually quartz is used as piezoelectric material. Disk-shaped quartzes with a thickness of

several hundreds of micrometers are the usual geometry. They are cut in a certain orientation (AT-cut), so that the vibration of the quartz is not an elongation, but a shear motion (Fig. 2.1) [17]. This enhances the sensitivity of the microbalances. A standard commercial microbalance has a ground frequency f_0 of several MHz. This resonance frequency depends on the geometry, i.e. the size and thickness, of the crystal:

$$f_0 = \frac{v_{tr}}{2t_q} = \sqrt{\frac{\mu_q}{\rho_q}} / 2t_q \quad (2.1)$$

Metal (or also carbon) electrodes are evaporated onto the quartz as electrodes. The combination of a potentiostat with an oscillator module allows to apply an alternating potential and also to perform electrochemical experiments.

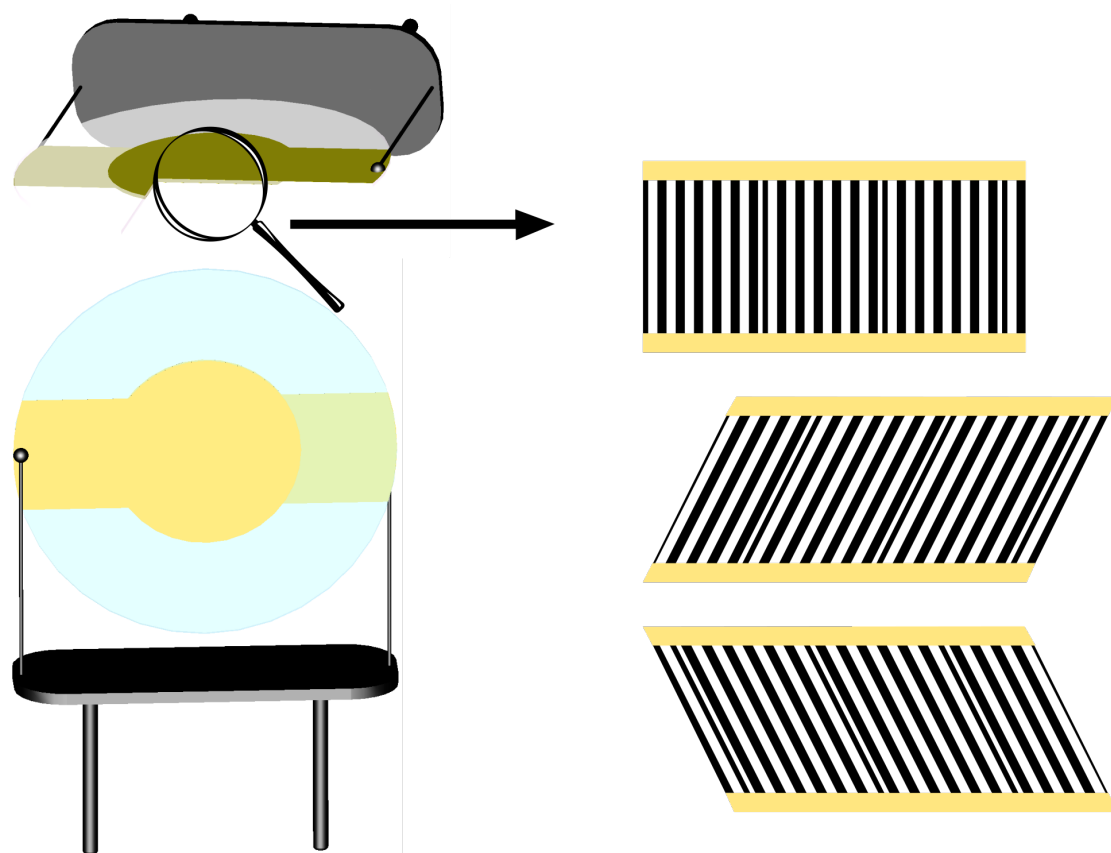


Figure 2.1: Schematic representation of an EQCM chip. A cross section shows the shear motion during operation.

Sauerbrey published in the mid of the last century his famous equation [88]. This relation between a shift in the frequency and a change in mass allows to quantify the deposited

mass in an *in-situ* electrochemical experiment.

$$\Delta f = -2f_0^2 \frac{\Delta m}{A\sqrt{\mu_q \rho_q}} \quad (2.2)$$

The signal, the shift in frequency Δf is proportional to the negative change in mass $-\Delta m$, This means a deposition would result in an increase in mass and cause a decrease in frequency. All other terms are constants. A is the area of the electrode, μ_q the shear modulus of the quartz and ρ_q the density of the quartz.

It shall be emphasized that the main challenge of EQCM experiments is the consequent interpretation of the data. A quantitative interpretation is insofar difficult, because the frequency is influenced by external factors. F.i., the temperature influences the parameters of the quartz and thus f_0 . Also the viscoelastic properties of the electrolyte play an important role. Models tried to describe this situation [97].

Many suppliers offer EQCM modules, which can also measure the damping. This can deliver additional information to the frequency shift and may help understanding the electrochemical mechanism better. A comprehensible example would be the observation of a roughening of the surface [50]. Rougher surfaces cause a decrease of the shift in frequency, because more solvent (i.e. mass) oscillates with the quartz. But, the damping of the oscillating quartz increases as well. Thus, this effect can be distinguished from smooth deposition quite easily.

2.3 Experimental

The detailed experimental procedures are described in the publication *In Situ FTIR and in Situ QMB Study of the Electrochemistry of Graphene Oxide on Platinum* [84], which is attached in Appendix A. In short:

GO was prepared by a modified Hummer's method [108] and cleaned by centrifugation. The experiments were performed in a Na-phosphate buffer solution (PBS) to vary and adjust the pH. A CH-Instruments 440A work station was used to perform EQCM measurements. Pt coated 8 MHz quartz wafers were employed. The electrode surface of the quartz oscillator was cleaned electrochemically in an aqueous H_2SO_4 solution.

The schematic setup of the *in-situ* FTIR spectrometry is presented in Fig. 2.2. A custom made Teflon[®] cell served as compartment. A conventional potentiostated three electrode

setup with a platinum CE and an Ag/AgCl RE (0.21 V vs. standard hydrogen electrode) was used. The Pt WE could be precisely positioned relative to the ZnSe window via a micrometer positioning system.

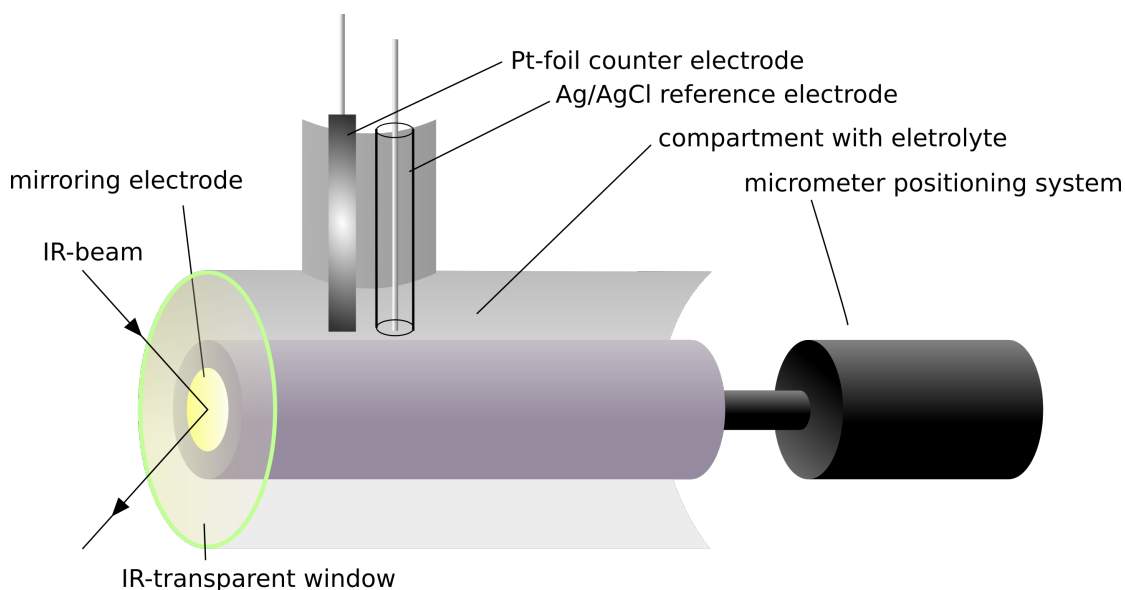


Figure 2.2: Schematic representation of the spectroelectrochemical setup

2.4 Results and Discussion

The identification of anodic and cathodic currents in this system was challenging. Thus, a lot of effort was put into this. All measurements were also performed blind, i.e. without GO, to distinguish between the electrolysis of the electrolyte and the electrochemical reactions of GO.

The results of the anodic potential sweeps are shown in Fig. 2.3. The upper graphs show the response of the QCM. The left graph shows a clear mass deposition (GO) between 1.5 V and 2.0 V. A comparison with a blind experiment (right graph) indicates that this mass deposition is related to GO, because in the case of the blind sample no significant mass change can be followed.

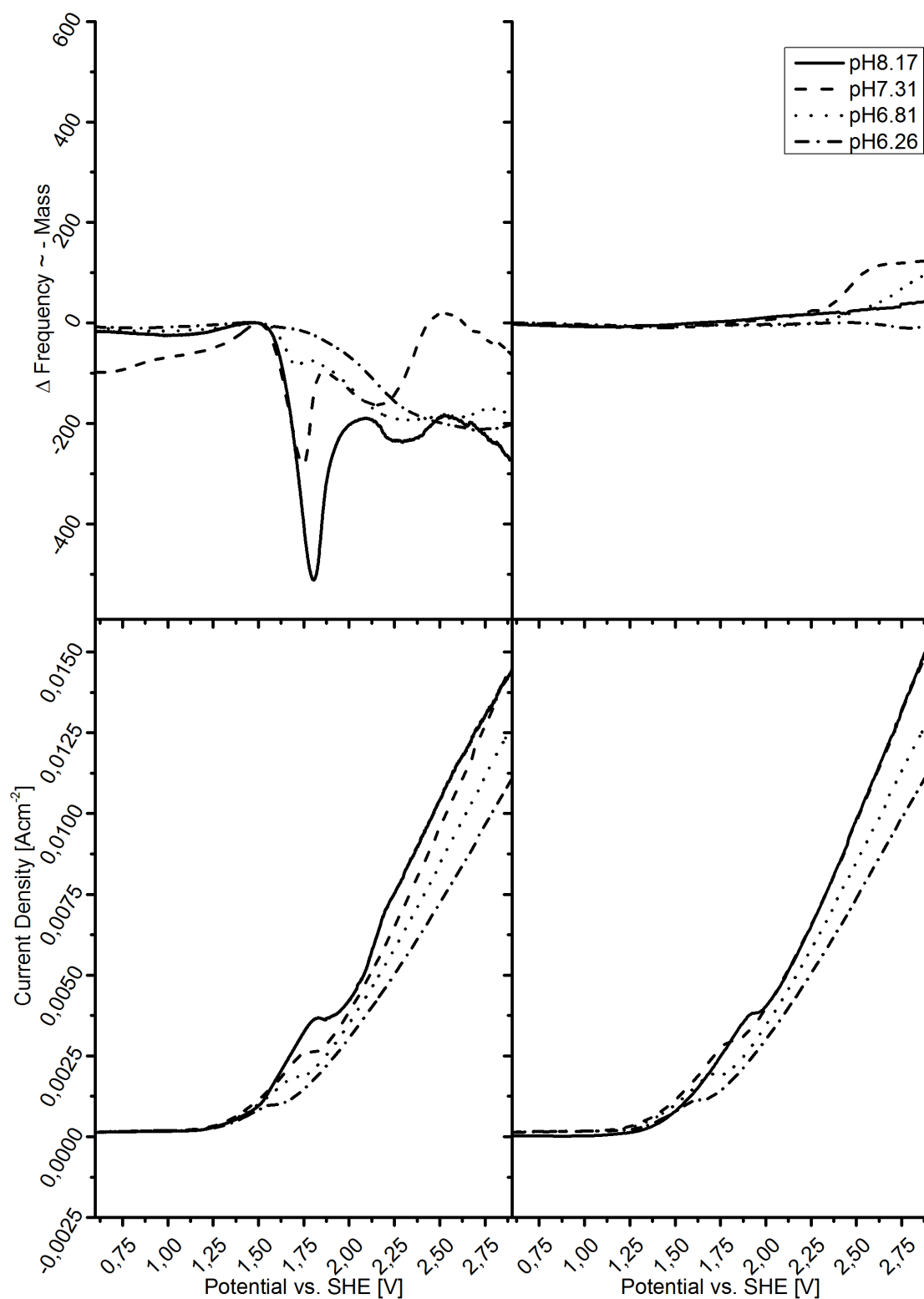


Figure 2.3: Linear anodic potential sweeps of GO dispersions on Pt. Left: with GO. Right: without GO. Up: potential dependent frequency (QCM). Below: potential dependent current.

It is remarkable that the mass deposition, i.e. the change in frequency, does not increase

with higher overpotentials. At a certain point the mass deposition stops and at even higher overpotentials all the deposited mass is more or less removed completely again.

Since the blind experiments do not show any mass changes, this can only be related to GO. GO is deposited at 1.5 V and desorbed at 2.0 V.

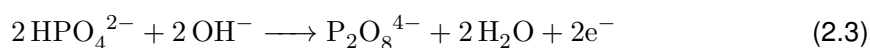
There is also a clear dependency of the GO deposition on the pH of the electrolyte. The most alkaline solutions show the strongest mass deposition and the most acidic solutions show almost no GO deposition. A possible explanation for that would be that GO is more deprotonated and therefore more negatively charged and thus better dispersible at higher pH. The positively polarized electrode may attract deprotonated polyanionic GO better.

A quantitative evaluation of the data can be done, but must be interpreted with care. The QCM signal is affected by many side effects, like f.i. the rigidity of the deposited film or the hydration water on GO. Assuming a perfect monolayer of graphene with a 2D density of $6.87 \cdot 10^{-4} \text{ g/m}^2$ (according to a bond length of 0.142 nm) [18], and the electrode surface of the used system of 0.196 cm^2 the theoretical frequency change would correspond to -99 Hz . Thus, it can be interpreted that the deposited films are maximum few monolayers thick.

The current-potential curves (Fig. 2.3 lower graphs) show that the GO adsorption concurs with the beginning electrolysis of water and generation of oxygen. This is also an explanation for the desorption of GO at higher potentials. The gas and bubble evolution repels the adsorbed GO flakes mechanically.

The second noticeable feature of these curves is a current shoulder right at the edge of the beginning gas evolution. These currents occur at the same potential range as the mass deposition, measured with the QCM. However, the same current shoulders can be seen at the blind experiments.

Thus, it can be concluded that these currents come from the electrolyte decomposition. A phosphate buffer solution is used in the experiments. Phosphate can be oxidized electrochemically in this potential range according to the following reaction. [45]



This oxidation of hydrogenphosphate to peroxodiphosphate is also pH-dependent. The reaction is favoured with increasing pH and thus the corresponding current shoulder increases. The reaction is driven by a higher concentration of the reaction partner OH^- .

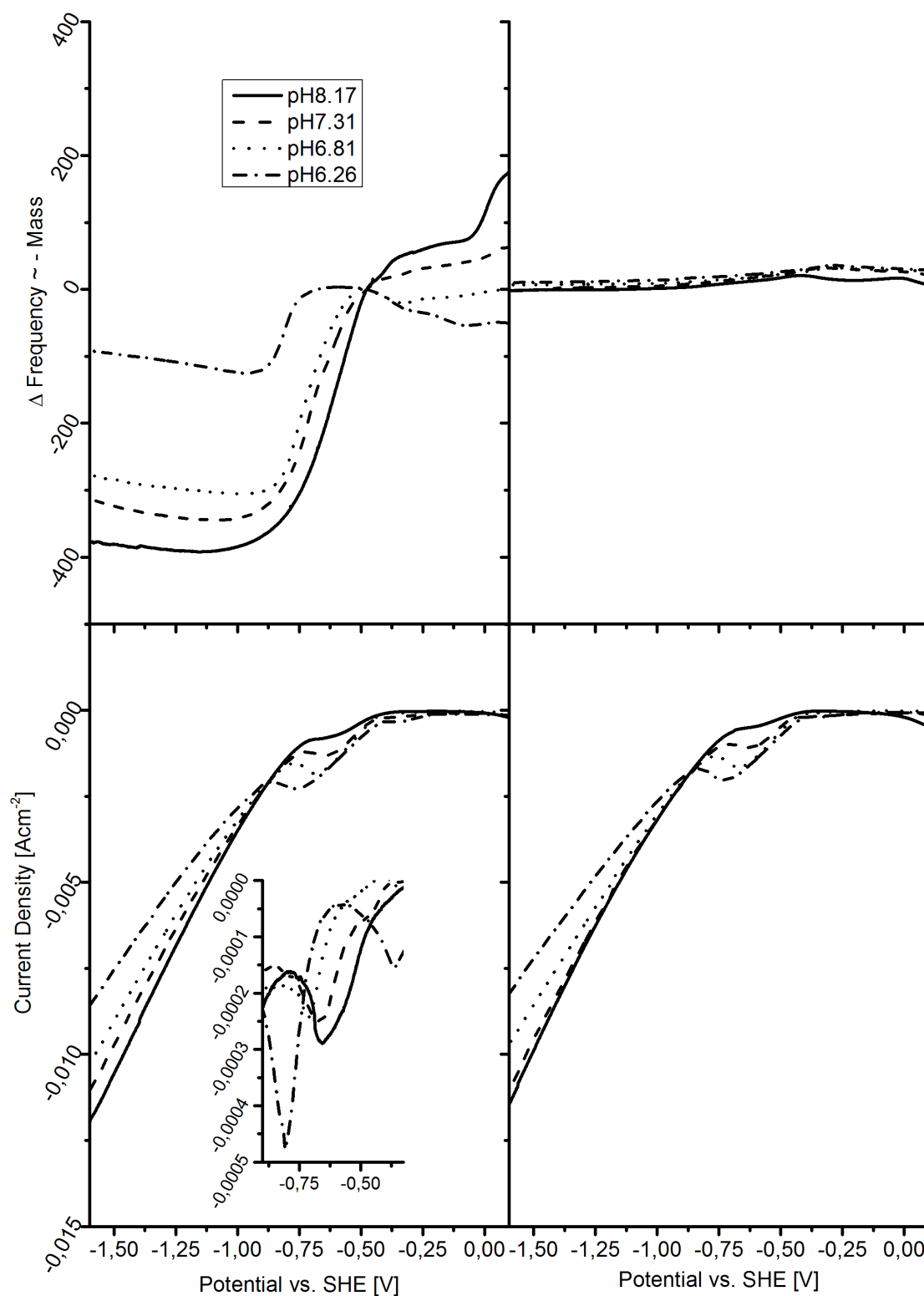


Figure 2.4: Linear cathodic potential sweeps of GO dispersions on Pt. Left: with GO. Right: without GO. Up: potential dependent frequency (QCM). Below: potential dependent current. The insert shows the difference of the measured current to the blind measurements.

The corresponding cathodic potential sweep experiments are shown in Fig. 2.4. The upper

graphs show again the frequency changes of the QCM measurements, whereas the lower graphs show the current potential curves. The right graphs are always the corresponding blind measurements to the left graphs, where GO suspensions were used.

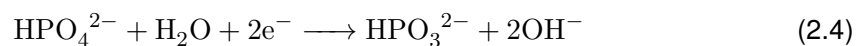
The QCM results show a different picture than in the anodic experiment. Again the blind measurements show no significant frequency change, but the deposition of GO follows another mechanism. The measured mass deposition starts at appr. -0.5 V and proceeds to appr. -0.9 V, depending on the pH.

As in the anodic deposition, the mass gain increases just to a certain overpotential. However, in contrast to the before mentioned experiment, the deposited mass does not decrease again, but it saturates. Obviously the cathodic mechanism differs from the anodic one. Here, the gas evolution does not remove the absorbed GO layer, but it prevents further adsorption. In the same potential range the electrochemical reduction of GO takes place [83]. This indicates that the mechanism of adsorption bases on the reduction of GO. RGO is less soluble than GO, because it lacks the polar oxygen functionalities. Therefore it may precipitate onto the working electrode as soon as it is formed and build a layer, strong enough to resist the gas evolution. Although, at some point the gas evolution will hinder further reduction and deposition of GO/rGO.

A pH dependency of the GO deposition was observed. The frequency change at higher pH is more significant. GO is less dispersible at lower pH [44]. Thus, it is less available and can be reduced more difficult.

The current potential curves show that the cathodic GO reduction and deposition takes place at the beginning hydrogen evolution. A current shoulder is located - similar to the anodic deposition - at the edge of the hydrogen reduction current. Since this shoulder is also present in the blind experiment, it can must come from the electrolyte decomposition.

Hydrogenphosphate can be reduced electrochemically to hydrogenphosphite [58, 95].



This current shoulder decreases with increasing pH, because the higher concentration of the reaction product OH^- decelerates the reaction.

Since we mentioned above that the deposition of GO bases on its electrochemical reduction, the corresponding current is expected in the current potential curves. The difference of the sample curves and the blind curves is shown in the insert in Fig. 2.4. Here, the expected reduction current becomes visible and relates concisely to the steps in the QCM results.

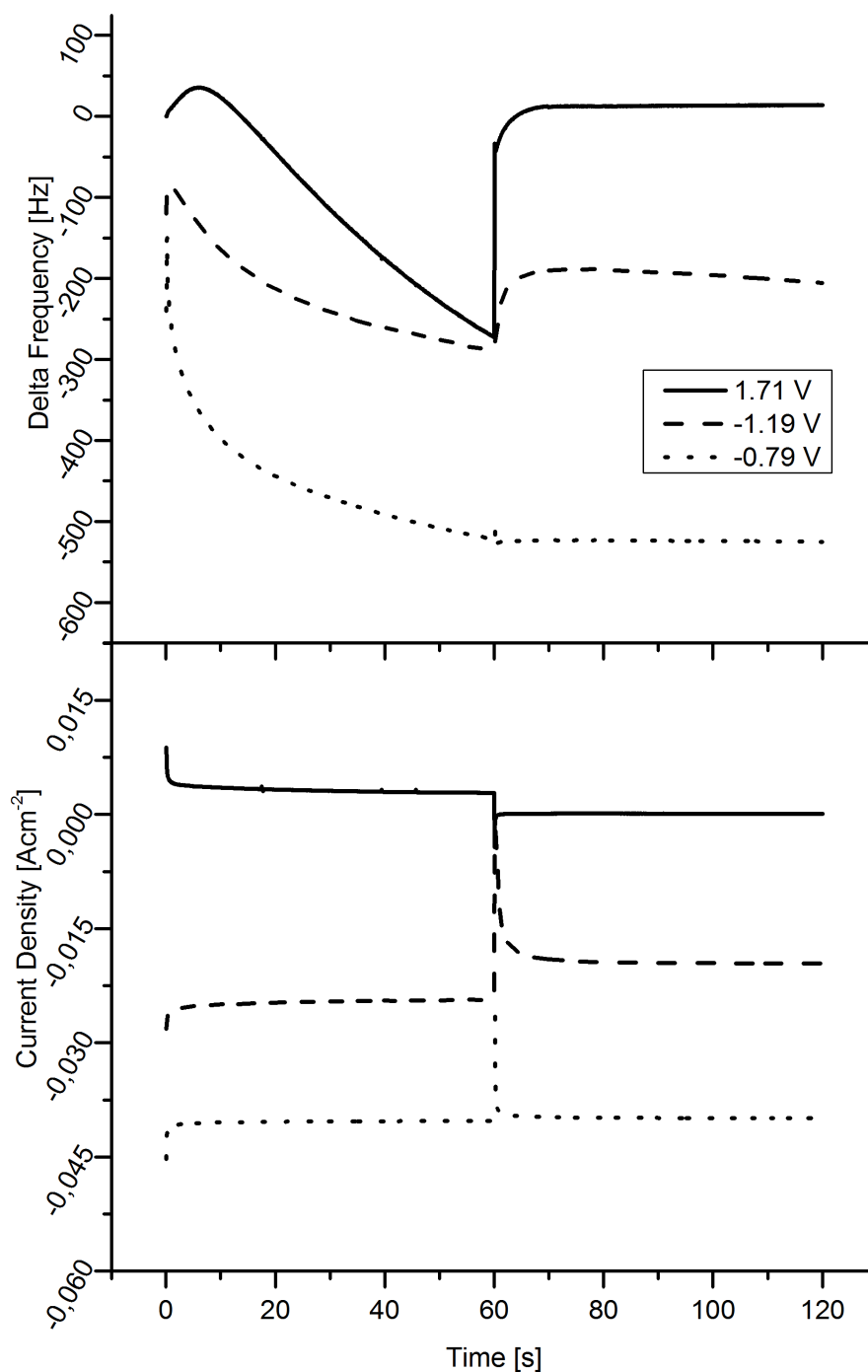


Figure 2.5: GO deposition at constant potential on Pt at different potentials for 60 s, followed by 60 s open circuit potential.

To validate the above mentioned assumptions about the mechanism of GO deposition, three potentials were chosen for investigating the deposition behaviour at constant potential. In the anodic case the experiment was performed at 1.71 V, the potential, where a strong

deposition was observed. The cathodic experiments used -0.79 V and -1.19 V, the potentials at the beginning GO deposition and after saturation. After 60 s of depositing GO, 60 s measurement at the open circuit potential followed.

The anodic deposition is displayed in Fig. 2.5 (solid line). As expected the deposition takes place at the constant potential of 1.71 V, which can be seen in the frequency decrease, detected by the QCM. However, as soon as the potential is switched back to the open circuit potential, all the deposited mass is desorbed immediately. This strengthens the theory that the forces binding GO to the electrode surface are of electrostatic nature, which only attract GO as long as the right potential is applied.

The cathodic mechanism is more complicated. When applying a potential of -1.19 V (Fig. 2.5, dashed line) GO gets deposited and stays at least partially on the electrode after applying the open circuit potential. GO is reduced electrochemically to rGO, which is poorly dispersible and precipitates thus onto the electrode. However, this process is impeded by the gas formation due to the electrolyte decomposition.

When depositing GO at a potential of -0.79 V (Fig. 2.5, dotted line) the picture looks different. The GO adsorption is - despite of less overpotential - stronger and after switching back to the open circuit potential, the complete deposited mass stays on the electrode.

The next question, which arose, was whether the phosphate electrolyte influenced the GO adsorption. It is conspicuous that in the anodic as well as in the cathodic case the adsorption takes place simultaneously with the phosphate reduction. To investigate this, phosphate was followed spectroelectrochemically via FTIR.

Fig. 2.6 shows the results of the electrolyte without GO. The upper graph shows the electrochemical results. As in the QCM experiments, a cathodic current can be seen at the edge of the hydrogen evolution (black line). After baseline fitting and integrating it over time, one gets the corresponding charge (blue line).

The lower diagram in Fig. 2.6 shows the course of selected peak areas over the potential. At 1080 cm^{-1} [60, 91] the symmetric P–O stretch vibration of phosphate can be followed. Phosphate was reduced at -0.5 V. The signal of H_2PO_3^- (990 cm^{-1}) increased in accordance with the respective redox reaction of phosphate to phosphite.

At an even more negative potential the signal of H_2PO_3^- decreased. At the same time the peak at 1030 cm^{-1} increases. This peak can be assigned to the asymmetric stretch vibration of the deprotonated form HPO_3^{2-} [38]. This can be interpreted that negative of -0.8 V, the pH increased above the pK_a of the couple $\text{H}_2\text{PO}_3^-/\text{HPO}_3^{2-}$ at 6.59 [47]. Therefore H_2PO_3^- gets deprotonated and its peak area decreases, whereas the one of HPO_3^{2-} increases.

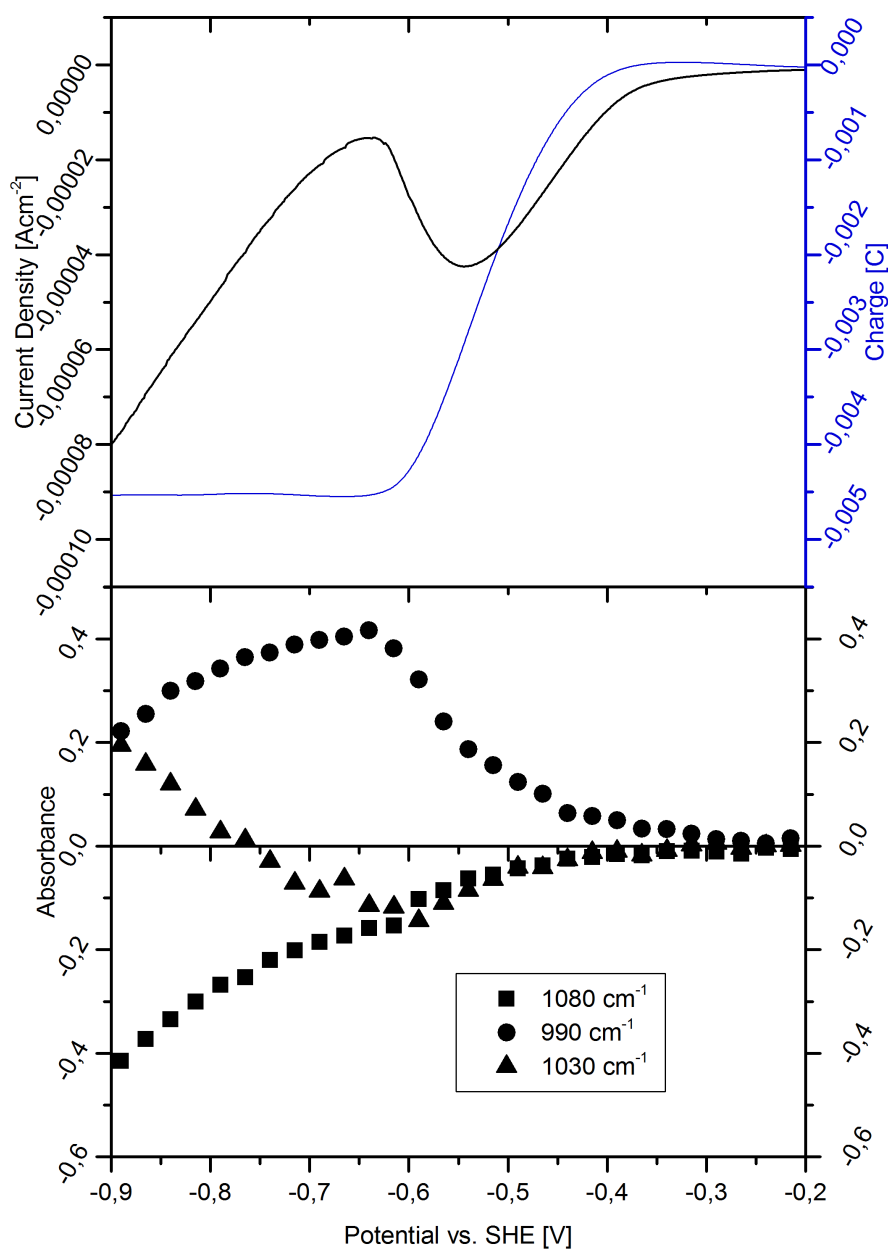


Figure 2.6: *In-situ* FTIR measurements of the cathodic reduction of the phosphate electrolyte without graphene oxide.

The same measurement were performed in the presence of GO in the solution (Fig. 2.7). Basically the same phenomenon could be observed. There is no hint that phosphate interacts in any way with GO. If this would be the case, one would observe at least a peak shift of the corresponding P–O stretch vibrations.

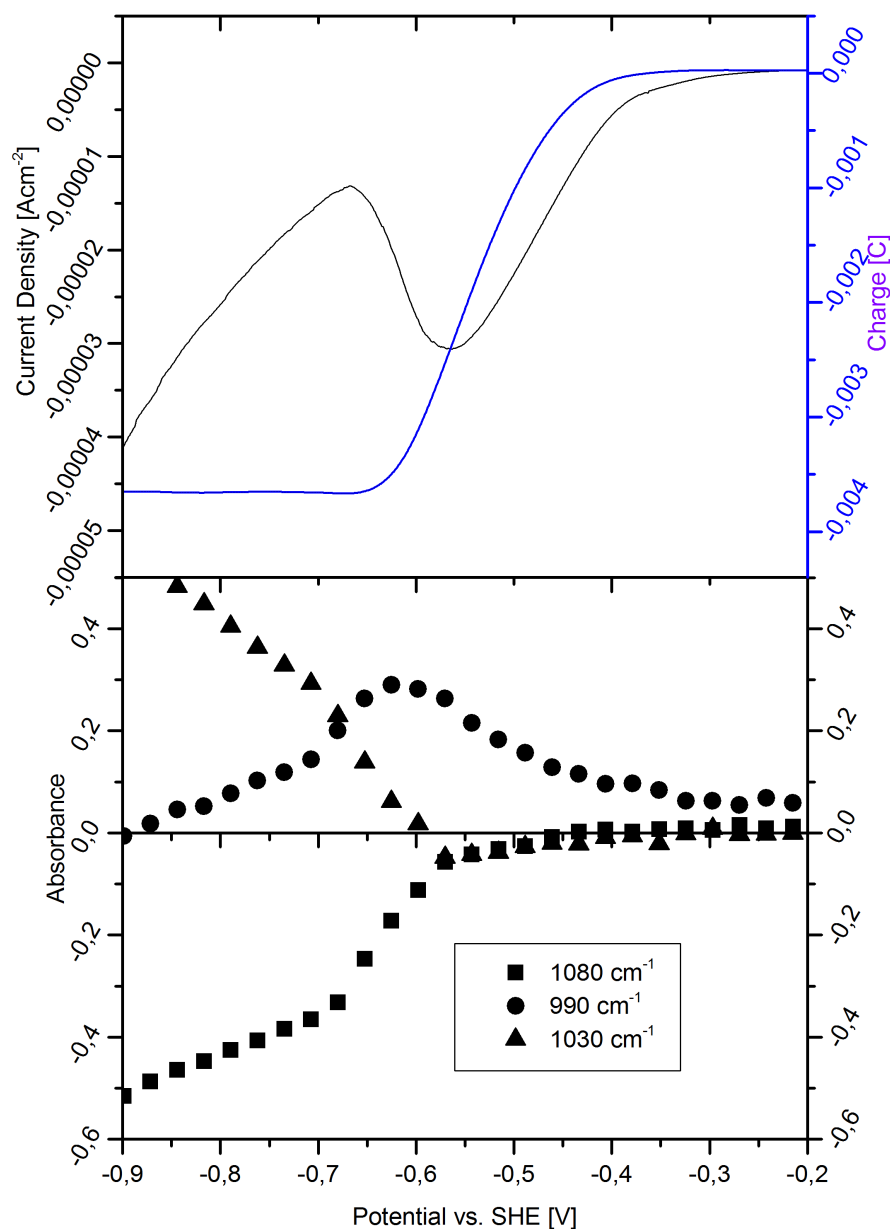


Figure 2.7: *In-situ* FTIR measurements of the cathodic reduction of the phosphate electrolyte with graphene oxide.

2.5 Conclusion

Mechanistic insights into the electrochemical deposition of GO on platinum were attained with the help of an EQCM. A phosphate pH buffer served as electrolyte. The working electrode was polarized anodically and cathodically. In both cases a deposition was possible, but the mechanism differs.

The electrochemical deposition of GO can be performed anodically in the range of 1.5 V and

1.8 V. The anodic adsorption of the GO polyanion occurs simultaneously with the phosphate oxidation. The GO adsorption is accelerated with increasing pH due to a better solubility of the anion sheets. Above 1.8 V, a GO mass decrease indicated the displacement of GO by oxygen gas formation due to the electrochemical decomposition of water.

The reduction in rGO and its deposition can be performed cathodically negative of -0.5 V at platinum. *In-situ* investigations showed that the reductive deposition of rGO takes place in parallel with the phosphate reduction and the hydrogen evolution at moderate overpotentials. Increasing the pH accelerates the adsorption of GO. The GO reduction is inhibited once a particular rGO film thickness has been reached. The hydrogen evolution persists in the interstices of these rGO sheets.

Chapter 3

Preparation of Graphene Oxide Coatings

3.1 Introduction

Although there is also the possibility of preparing free standing GO films [21, 31], most publications focus on the preparation of GO coatings [34, 35, 64, 89, 92, 93, 108]. The choice of the right technique for preparing GO coatings is important for forming a uniform film with reproducible and controllable properties, like f.i. thickness, structure, or oxidation degree.

The easiest way for preparing GO coatings is just drying a droplet of GO suspension on the desired surface [14, 70, 105, 106]. Because of the easiness of this technique and the fact that no expensive equipment is required, it is relatively often used. However, the reproducibility and also the quality of the results are poor. People tried to find a routine for improving the reproducibility of this technique, but in comparison to others it is still bad. The thickness of the layer can be partially controlled by adjusting the GO concentration in the used suspension. For that either a micro pipette is used to transfer a defined volume of GO and the temperature of the substrate is controlled. Or, automatized machines are used.

A better controllability of the coating can be obtained by the electrochemical deposition of GO [84], which is described in detail in chapter 2. In this one-step approach the desired thickness of the layer can easily be adjusted by the time of deposition. However, a concurrent electrochemical reduction of GO takes place together with its deposition. Thus, it is not possible to obtain GO coatings, but only rGO coatings.

An example for an automatized coating technique would be spray coating [114]. In several steps GO is sprayed onto the sample and dried by an IR-lamp. This allows the coating of large areas with relatively high homogeneity and reproducibility. Also the final thickness can be adjusted.

A related technique is inkjet printing [33]. A special ink of the GO suspension has to be prepared. This needs accurately defined properties to be applicable in an inkjet printer. The great benefit of this technique is that predefined patterns can be created.

In spin-coating, a disk shaped sample is rotated at a defined speed, while a solution (the GO dispersion) is spreaded on the sample. The thickness of the coating can be adjusted by the viscosity of the liquid and the rotational speed of the substrate. The liquid must wet the substrate for this process. Therefore, this can be easily done with aqueous solutions on hydrophilic substrates, like SnO_2 [56] or a silicon waver [55], but not on hydrophobic substrates like gold.

For preparing monolayers, a self-assembling technique would make sense. Usually for this

a linker molecule must be chosen between the substrate and GO. For this 2-mercaptoethylamine [103] and 4-mercaptophenole [83] were proposed. In both cases a mercaptogroup binds to a gold substrate, whereas an aminogroup or an alcoholgroup should bind to GO. The binding of the mercaptogroup to gold is generally accepted. However, the final proof for the chemical bond to GO still has to be done.

After coating a substrate its characterization is of importance. One big question is the determination of the thickness of the coating. Ferrari [37] showed that for CVD graphene the 2D peak of the Raman spectrum has a characteristic shape for up to five layers. Thus, it is possible to count the number of graphene layers by calibrating the Raman spectra. For more than five to ten layers the spectra cannot be distinguished from graphite anymore.

Many groups characterize the coating by AFM [34, 43]. The high sensitivity of an AFM make it possible to visualize single graphene flakes. It is also possible to investigate the structure of the sheets, whether they are separated, folded, or stacked. However, if the layers are thicker than a monolayer and cover the hole surface, it is not possible anymore to make assumptions about the thickness of the layer.

3.2 Experimental

3.2.1 Preparation of the Substrates

As mentioned in the introduction it is obligatory for spin coating that the liquid wets the substrate. In this work only aqueous and alcoholic GO suspensions were used. Thus, the substrate surface must be hydrophilic. The used substrate materials were glass, ZnSe, and gold. Except for the gold sample all samples were hydrophilic and could be used as they were.

The Au samples were built as shown in Fig. 3.1. A conventional microscope glass slide functioned as substrate. By physical vapour deposition 50 nm of Ti were evaporated onto the glass followed by 50 nm of Au. The role of Ti was as adhesive layer to improve the mechanical stability of the coating. Au adheres itself poorly to glass.

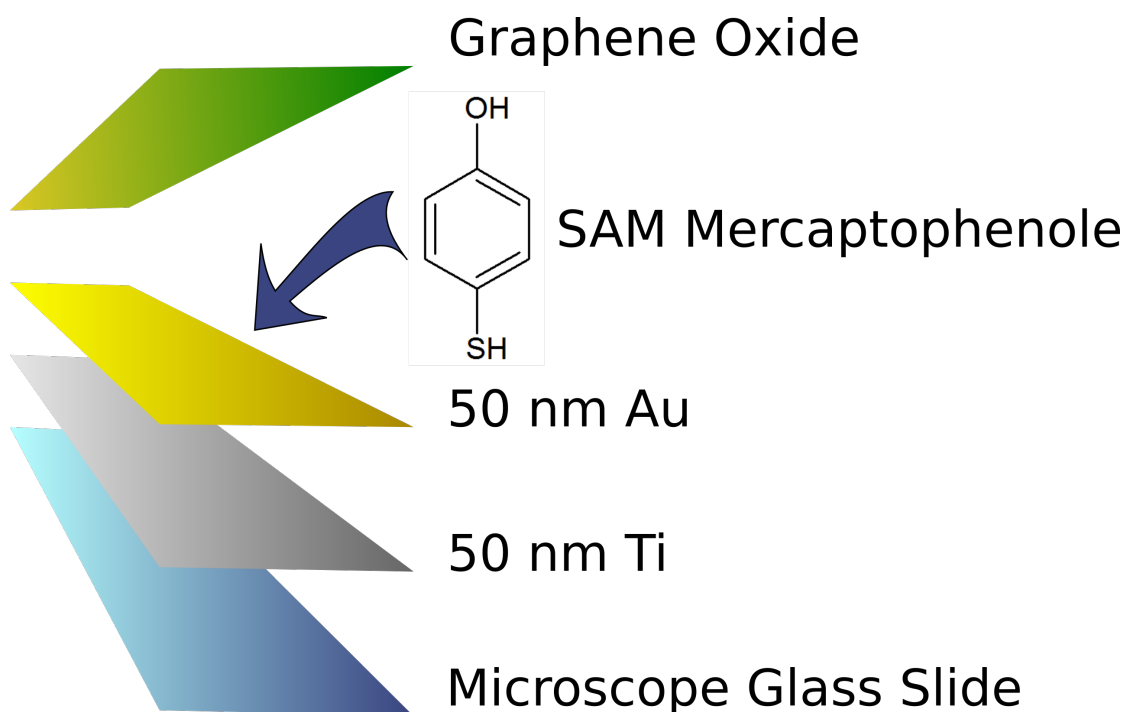


Figure 3.1: Schematic structure of the prepared GO coated Au samples.

In a next step the sample was coated with a self assembled monolayer of 4-mercaptophenol. To do so, the sample was soaked into a 2 mM solution of 4-mercaptophenol in ethanol. After 24 h it was rinsed with ethanol and dried under an Ar jet.

Contact angle measurements were performed with a Krüss DSA 30. As prepared Au coated glass slides were used. As testing solutions GO suspensions were prepared. GO was obtained from Graphene Laboratories Inc. Suspensions with a concentration of 6.2 mg/ml were diluted in a 1 : 6 volume ratio with water and ethanol at different ratios.

3.2.2 Spincoating

Usually spincoating is only possible for flat circular substrates. If, like it will be discussed in course of this thesis, it is necessary to coat a more sophisticated geometry like a prism, another substrate is coated in a first step and afterwards the coating is transferred to the prism. This process is challenging and in many cases not possible. Therefore it is much more straightforward to coat the prism directly.

To do so adapters were produced with a 3D printer (Ultimaker B.V.; model Ultimaker²), which had an embedding for the sample and a circular symmetry fitting onto the vacuum chuck of

the spin coater (Fig. 3.2). With this routine almost any sample geometry could be directly coated with the spin coater as long as the sample fitted in its chamber.

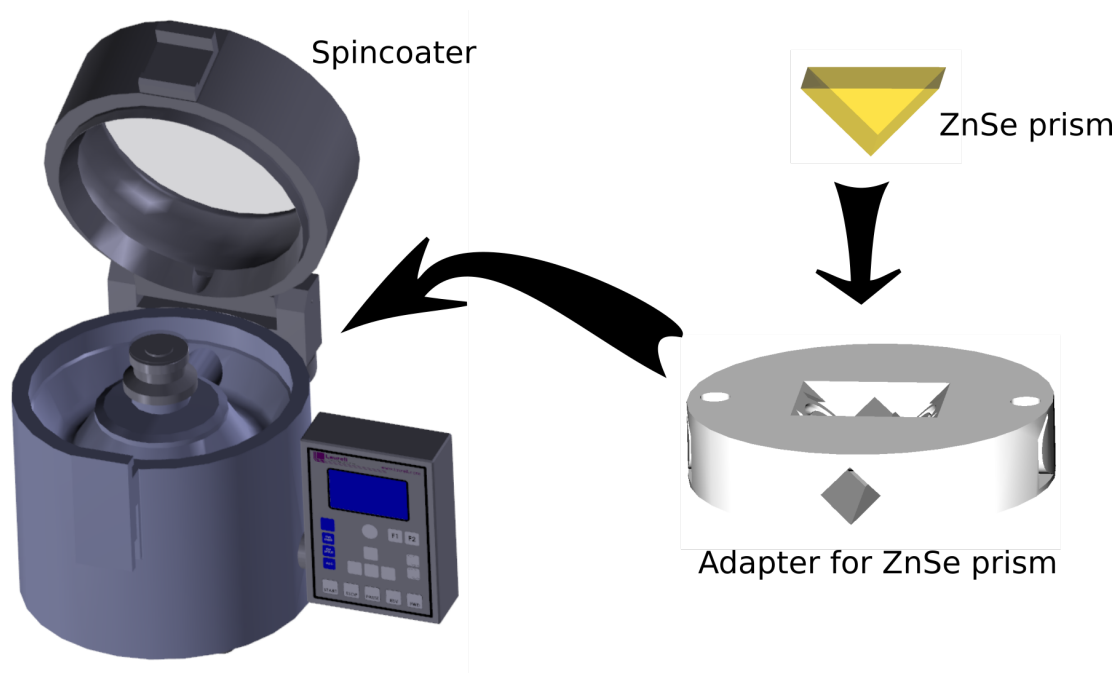


Figure 3.2: Custom designed adapters for the spincoater, produced with a 3D printer, made it possible to coat almost any sample by spin coating.¹

A Laurell Model WS-650S-6NPP/A1/AR1 spin coater was used. GO coatings were applied in several coating steps, whereas one coating step consisted of a 5 s initial phase at a speed of 200 rpm, applying of the suspension for 2 s at 200 rpm, and drying for 20 min at 600 rpm.

3.2.3 Determination of the Graphene Oxide Coating Thickness

The detailed description of this process was published in *A Multivariate Curve Resolution evaluation of an in-situ ATR-FTIR spectroscopy investigation of the electrochemical reduction of graphene oxide* [83], see appendix B. In short:

A femtosecond pulse laser was used to generate a defined groove in the GO coating on the spin coated samples. The depth of these grooves was measured with a scanning force microscope in contact mode at constant force.

¹3D model of the spincoater from <http://www.laurell.com/> [2017-11-16]

3.3 Results and Discussion

3.3.1 Preparation of Graphene Oxide Coatings

To produce homogeneous GO coatings, the GO-suspension must wet the hydrophobic gold surface. Two approaches can be followed to reach this goal. Either the properties of the liquid or the properties of the surface must be optimized. The first optimization was done with the GO suspensions (Fig. 3.3, red bars). An addition of ethanol to the water suspensions improved the wetting behaviour.

The figure shows that the contact angle and thus the wetting behaviour increased with higher volume ratios of ethanol. However, it was a not complete wetting and since it must be considered that the content of ethanol will decrease during drying, this result was not satisfying. For further improvement of the wetting behaviour, a 4-mercaptophenole SAM was prepared on the Au surface and led to complete wetting already at a volume ratio of ethanol/water of 67/33 (Fig. 3.3; green bars). Therefore, 4-mercaptophenole self assembled monolayers were applied to all Au surfaces throughout this study. This allowed the use of Au samples also during spin-coating, where one has to consider that the ethanol/water ratio changes during the process.

There are discussions about a self assembled monolayers of GO, where similar linker molecules were used [103]. It is possible that also in this case GO bonded via an ester bond over 4-mercaptophenole to the Au surface. However, we do not have any proof for that, since our main focus was adjusting the wetting behaviour of the spin coating solutions on the Au surface.

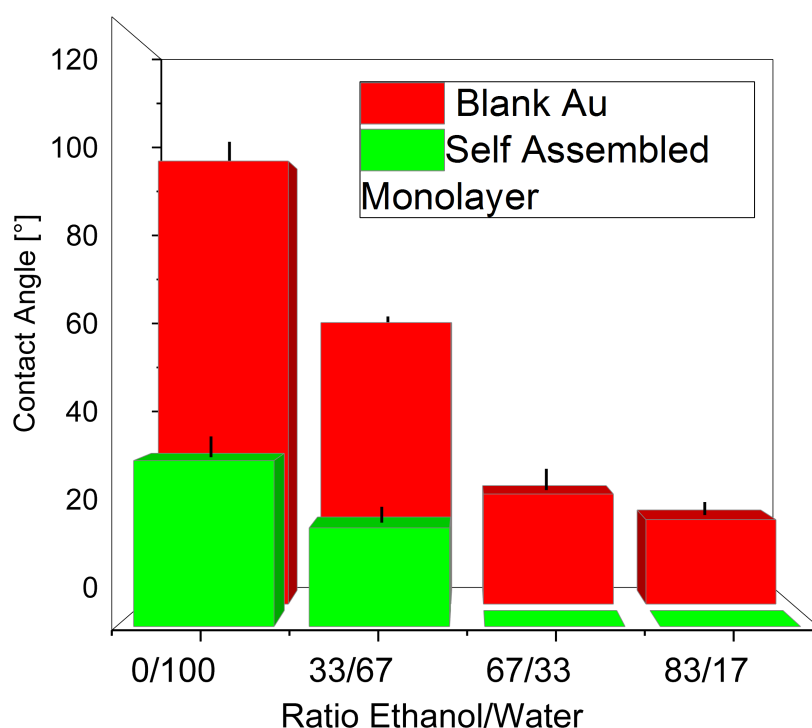


Figure 3.3: Contact angle measurements of GO suspensions at different ethanol/water ratios. Red bars: measurement on Au surface. Green bars: measurement on Au surface with self assembled monolayer mercaptophenole.

3.3.2 Thickness Measurements of the Graphene Oxide Coatings

Fig. 3.4 shows a laser-generated groove in a GO coating. The open source software *Gwyddion* was used for evaluating the AFM images. Although the roughness of the samples was relatively high - compared to the depth of the laser grooves - it was possible to average over a representative areas and determine the thickness of the GO coatings. The thickness of the coatings was determined to be ca. 3 nm per coating step, which corresponds to three GO single layers (assuming one GO sheet with a 1.1 nm thickness [43]).

The AFM image in Fig. 3.4 also shows the layered structure of GO. In the lower right corner a single sheet is marked with white dots. A close look shows that the whole layer is built out of these layered structure. The laser groove cuts through them. In the profile these sheets cannot be observed. An expected height difference of roughly 1 nm is too small to be detected. However, in the overall picture of the image it can be clearly seen.

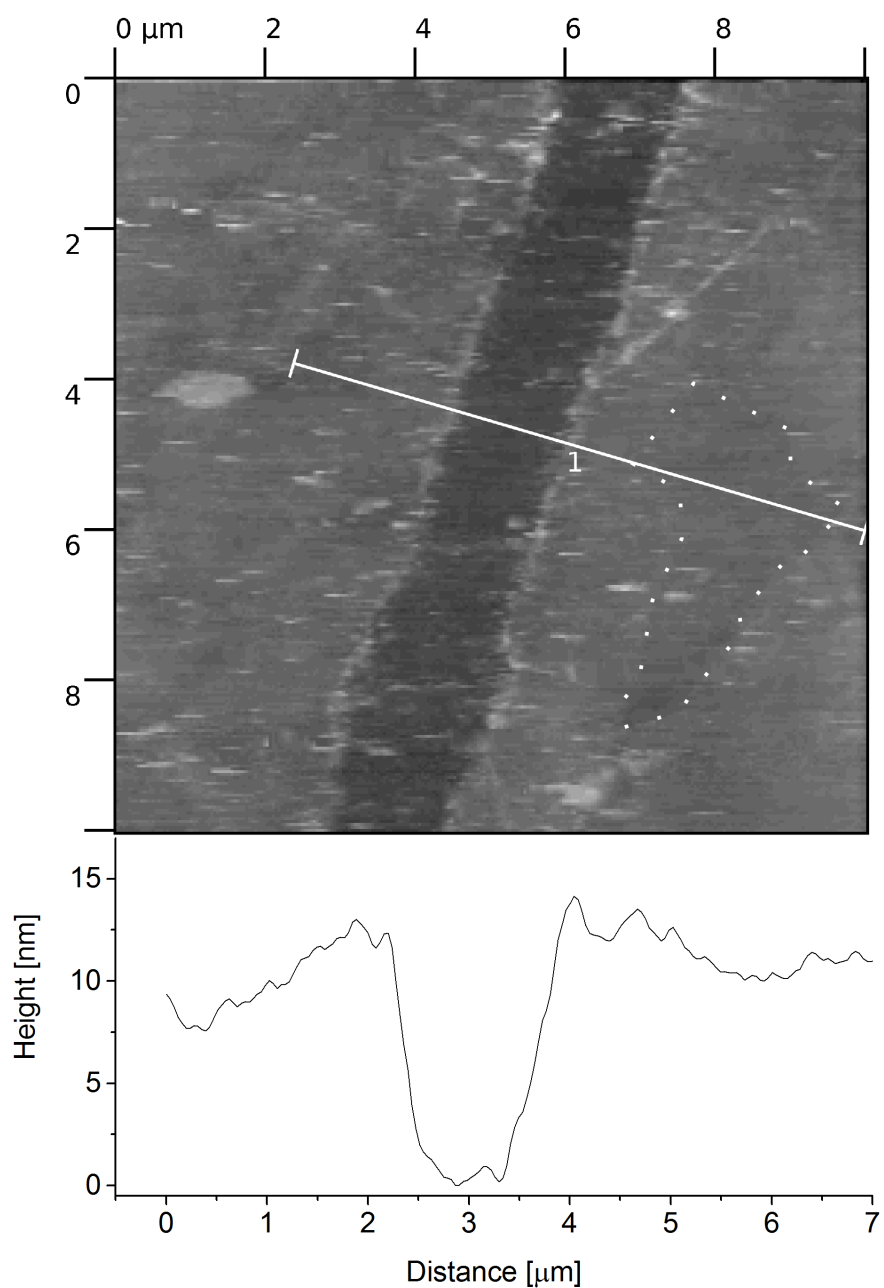


Figure 3.4: On top: Exemplary AFM picture of a laser groove in a GO coating. Below: Height profile of the marked white line in the picture above.

The results of three different thicknesses are shown in Fig. 3.5. The linear regression shows

a slope of 3.0 ± 0.6 nm, which means that each coating step led to 3 nm. Four coating steps were applied on the samples for the *in-situ* measurements. 12 nm thick layers, which were used for further investigations in this thesis, corresponded to 11-12 GO sheets.

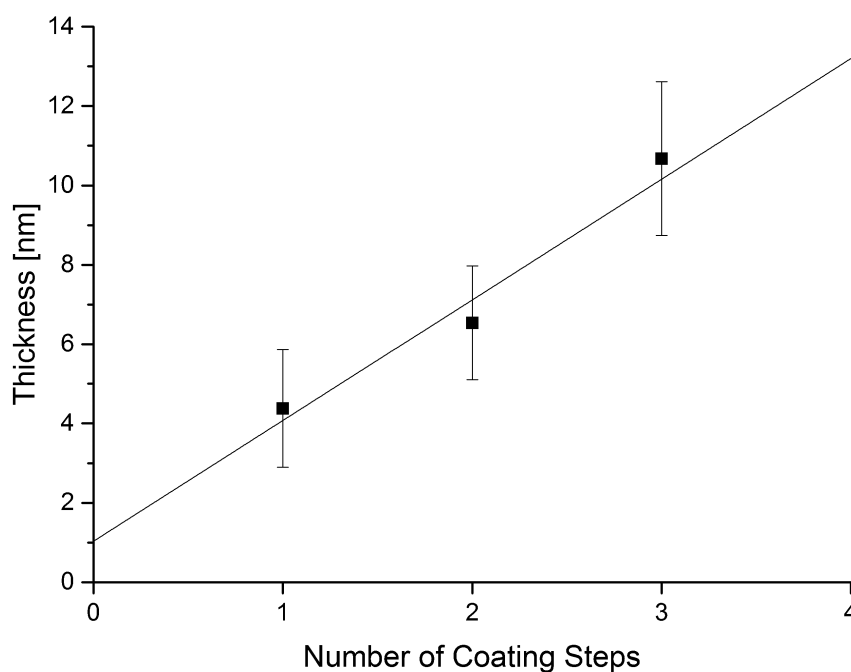


Figure 3.5: Measured thickness of the GO coatings vs. the number of spincoating steps. One spincoating step corresponds to one time of applying the GO suspension and drying.

3.4 Conclusion

The most performed route for producing GO and rGO coatings is the 2-step approach, where the sample is coated with GO in a first step, which is then modified - f.i. electrochemically reduced - in a second step. This requires a preferably versatile and reproducible routine for preparing GO coatings.

We decided to prepare our coatings via spincoating. To be able to coat various, also non circular, samples, custom adapters were designed and produced with a 3D printer for many different sample geometries. This reduced the geometrical requirements and limitations for the samples drastically. The samples only needed a flat surface, a symmetry that allowed to embed it into a balanced adapter, and it had to fit into the chamber of the spincoater.

The second problem to solve was that the GO suspensions did not wet the Au surface,

which was an interesting electrode material. To overcome this, ethanol was added to the GO suspensions and a self assembled monolayer of mercaptophenole was prepared on the Au surface.

Finally the thickness of the GO layers had to be measured and quantified. A femtosecond laser served for cutting a groove into the GO coating. This groove was imaged with an AFM and its depth was evaluated. One coating step resulted in 3 – 4 nm GO coating, where one GO single layer corresponded to appr. 1 nm.

Chapter 4

Graphene Oxide Reduction with a Femtosecond Laser

4.1 Introduction

The photoreduction of GO is a powerful technique, because it enables the reduction of GO in a desired pattern, is reproducible, and can be performed in air. There are reports on the photoreduction of GO on solid surfaces, as well as in suspensions. The light sources for this process reach from sunlight [7] over UV-lamps, flashlights [27, 40], cw-lasers, ns-pulse lasers, to even a fs-laser [111, 113].

It was suggested that the reduction mechanism, either photothermal or photochemical, depends on the experimental parameters, especially the light source [113]. The deoxygenation of GO occurs already at very low temperatures of less than 100 °C. The energy of a flashlight deposited in the GO coating by light absorption was calculated to be sufficient to heat GO and trigger its reduction [113]. The photochemical reduction bases on the generation of electron-hole pairs [66, 113]. They play the central role in the reduction of GO. Fig. 4.1 shows a scheme of the mechanism of this process. The generated hole reacts with a sacrificial reductant. Water is formed out of –OH functionalities. The aromatic system is regenerated. Also the elimination of CO₂ may occur. [26, 66]

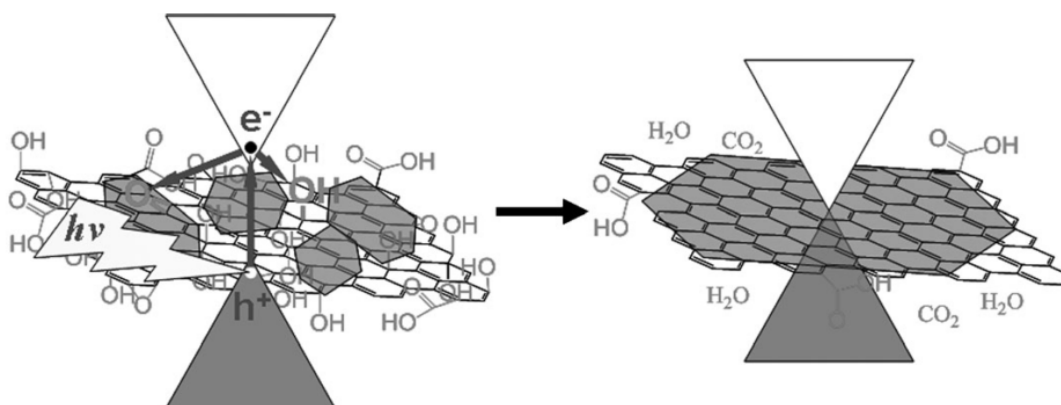


Figure 4.1: Mechanism of the Photoreduction of GO. Reproduced with permission [66].

With a fs-laser as light source, it is assumed that a combination of the photothermal and photochemical mechanism occurs [113]. The molecular mechanism of the fs-laser-induced reaction still remains an open question [111].

In this work a Ti:Sapphire fs-laser was used to reduce GO coatings on Au and glass substrates at different laser fluences. The influence of the fluence and the substrate was discussed. A Raman microscope and a scanning electrochemical microscope were utilized for

characterizing the samples.

4.2 Experimental

GO was spin coated onto conventional microscope glass slides, either Au coated or uncoated. The procedure is reported in section 2. Four coating steps were applied. Thus, the final layer thickness was approximately 12 nm.

These samples were irradiated using a Ti:Sapphire Chirped Pulse Oscillator (modified Femtosource XL, Femtolasers Produktions GmbH), which was delivering pulses with a full width half maximum duration of 60 fs at a central wavelength of 800 nm and a repetition rate of 11 MHz. A research microscope (Zeiss AxioImager.M1 equipped with a Zeiss EC Plan-NEOFLUAR 10x/0.3 objective) was used to guide the beam onto the samples. For the determination of the focus a custom system was used, which is described elsewhere [8]. Different laser fluences were used to reduce the GO coatings. The samples were scanned over a region of $200\text{ }\mu\text{m} \times 1000\text{ }\mu\text{m}$ each line shifted by $1\text{ }\mu\text{m}$. The scan speed of the stage was adjusted to 10 mm/s, which resulted in a total number of 9240 pulses/spot.

The characterization of the samples was carried out with a Raman microscope (WITec alpha 300A; excitation wavelength: 532 nm; laser power: 0.1 mW) and a scanning electrochemical microscope (SECM, CHI920D) using a 1 mM FcMeOH and 100 mM KNO_3 aqueous solution.

4.3 Results and Discussion

Microscope images of rGO are shown in Figs. 4.2 and 4.3. The different fluences of the laser resulted in different colours of the reduced pattern. It can be assumed that there are two important fluence thresholds. At the first threshold, GO is reduced to rGO. At the second threshold at higher fluences, GO and/or rGO is ablated.

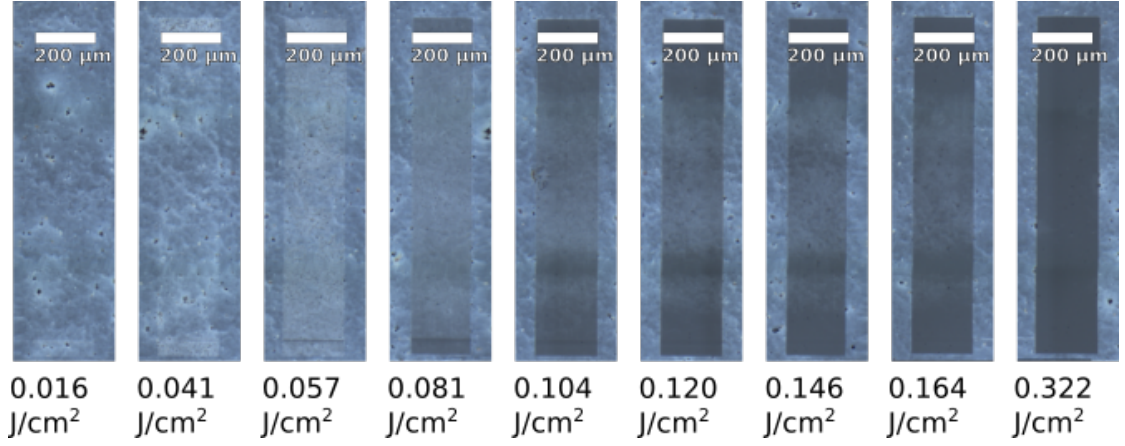


Figure 4.2: Microscope image of the rGO areas on a glass substrate, generated with a fs-laser at different fluences.

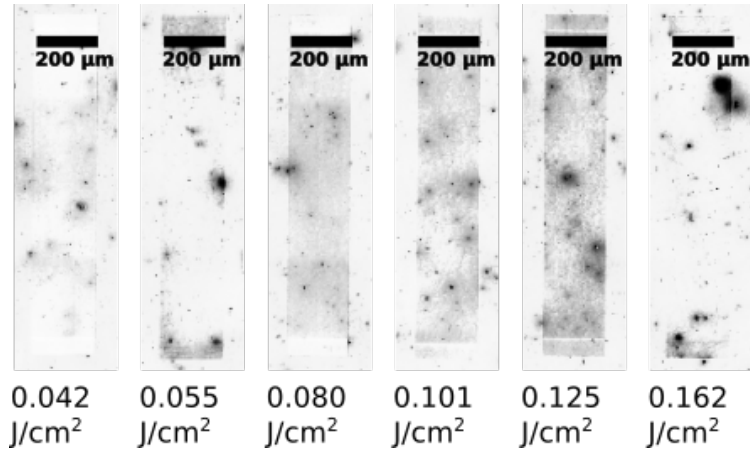


Figure 4.3: Microscope image of the rGO areas on a Au substrate, generated with a fs-laser at different fluences.

The reduction of GO can be recognized by a reduction of the reflectivity (microscope lamp) on the Au substrate, and an increase of the reflectivity on the glass substrate. In both cases the reduction threshold was $F_{th,r} \leq 0.05 \text{ J/cm}^2$. On the glass substrates at 0.016 J/cm^2 no modification can be seen. On Au at 0.042 J/cm^2 a minor colour change can be noticed. The ablation can be observed, when the substrate starts shining through the GO coating. In the case of Au brighter areas can be seen, because the microscope light is reflected better. On glass darker areas evolve, less light is reflected, but shines through the glass slide. The ablation on Au starts at $F_{th,r} = 0.101 \text{ J/cm}^2$ and on glass at $F_{th,r} = 0.081 \text{ J/cm}^2$. This shows that a limited fluence window is provided for the laser-induced reduction due to a rather low ablation threshold.

A more quantitative evaluation of the extent of reduction was undertaken by Raman spectroscopy. Fig. 4.4 shows the Raman spectra of GO and the reduced rGO regions at different

fluences on glass. The intensity of the spectra decreases at higher laser fluences. From 0.164 J/cm^2 upwards no carbon species can be detected any more. At this fluence GO/rGO is completely ablated. However, the ablation of GO/rGO starts already at lower fluences and proceeds continuously in both cases, on Au and on glass. This shows the microscopic images, as well as the absolute intensities of the spectra. The strong D and G bands indicate small crystal sizes [24].

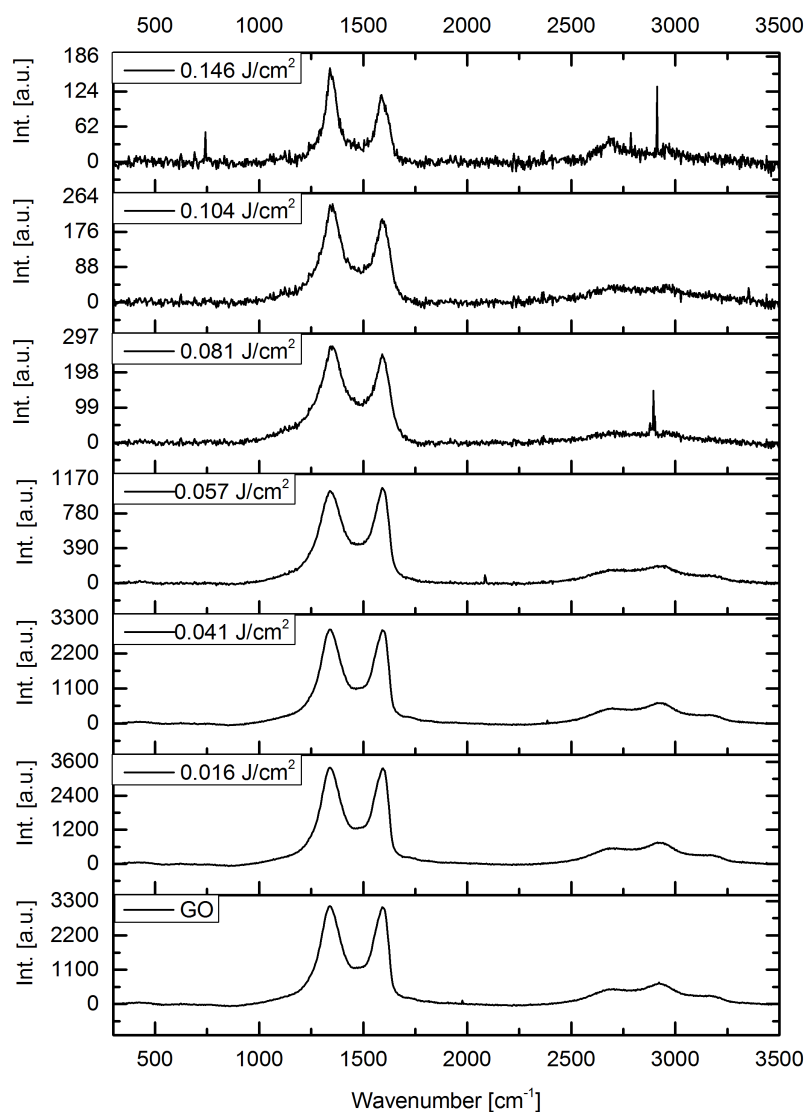


Figure 4.4: Raman spectra of GO/rGO on glass. The different spectra are related to the used fluences of the fs-laser for the GO reduction.

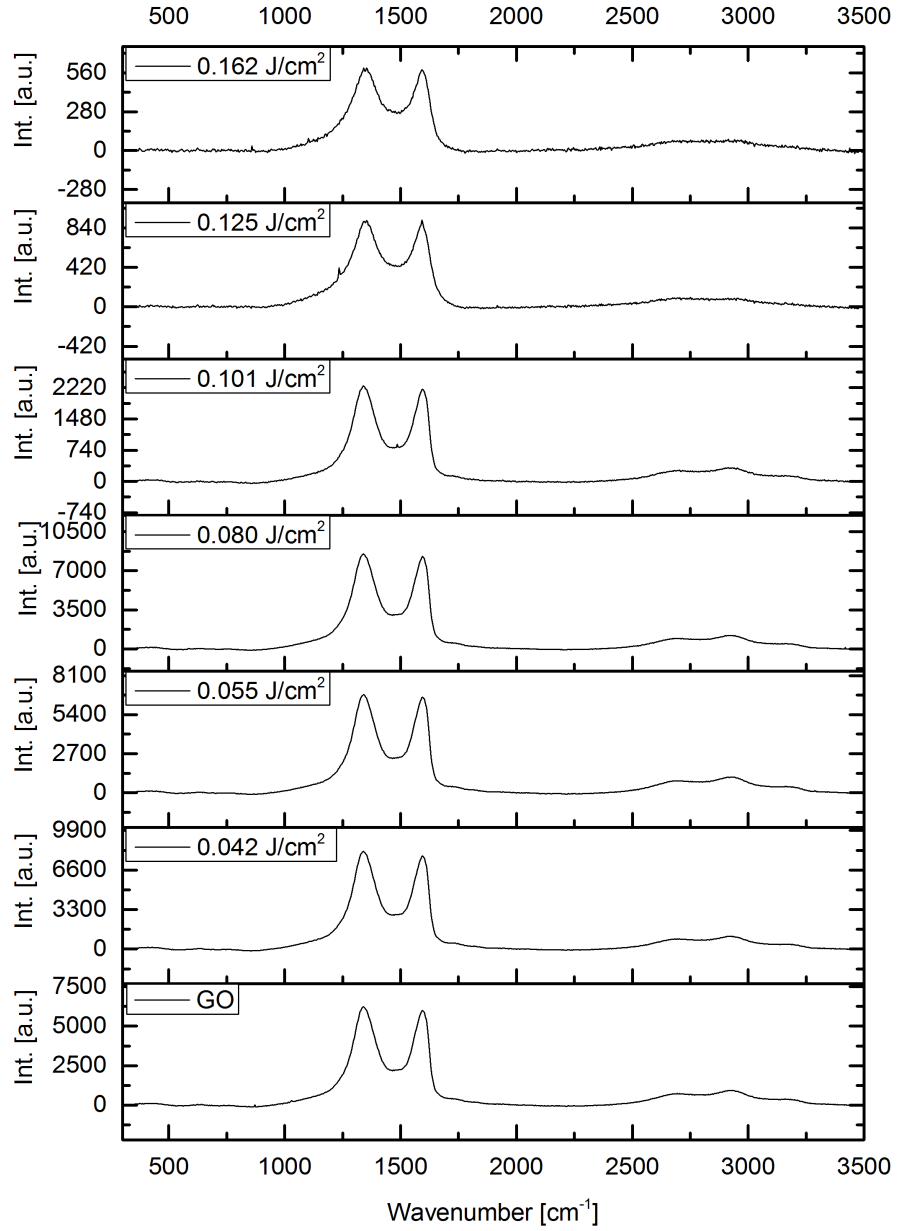


Figure 4.5: Raman spectra of GO/rGO on gold. The different spectra are related to the used fluences of the fs-laser for the GO reduction.

The analogous figure, containing the spectra of fs-laser reduced GO on Au is shown in Fig. 4.5. Also here the intensity of the respective Raman peaks decreases with higher laser fluences for the GO reduction.

4.3.1 The Ablation Behaviour of GO/rGO

The ablation threshold of GO/rGO $F_{th,a}$ is an important parameter for further considerations. The microscopic images of the treatment on glass (Fig. 4.2) showed that at 0.322 J/cm^2 no

carbonaceous species could be detected any more supported by a zero signal in Raman. The absolute intensities of the G and D bands are presented vs. the laser fluences in Fig. 4.6b and Fig. 4.6c. Ablation thresholds can be derived for glass $F_{th,a} = 0.04 \text{ J/cm}^2$ and for Au $F_{th,a} = 0.08 \text{ J/cm}^2$. As it is discussed later, the ratio of the G and D bands changes, however, in an negligible extent compared with the absolute values.

The reflectivity of the irradiated areas of the microscope images (Fig. 4.2 and Fig. 4.3) was evaluated (Fig. 4.6a). On the glass substrate the brightness increases between 0.041 J/cm^2 and 0.057 J/cm^2 . The sample illuminated at 0.057 J/cm^2 shows a metallic shimmer due to the presence of rGO. Above 0.057 J/cm^2 , the reflectivity decreases because of the ablation of the GO/rGO coating. Light penetrates the thinner rGO coating and the underlying glass slide which shows negligible reflection.

The process on Au appears differently. Between 0.055 J/cm^2 and 0.101 J/cm^2 the reflectivity of the coating decreases drastically because Au covered by an increasing amount of rGO shows less reflectivity. At 0.162 J/cm^2 , the reflectivity returned to the value of the Au covered by the transparent GO because of almost complete ablation of the film.

4.3.2 Defects in GO/rGO

The band ratios can be informative about the defects in GO/rGO. A comparison of the prominent D and G bands can provide information about the density of disorder in the carbonaceous species. Since the G-band originates from in-plane sp_2 vibrations and the D band from structural defects, the $I(D)/I(G)$ ratio is a measure for the amount of disorder in the structure [24]. The D peak itself is only visible, when defects are present. It bases on the excitation of a charge carrier, which is inelastically scattered by a phonon, followed by a second elastic scattering by a zone boundary or defect [24].

The spectra show that during the reduction the $I(D)/I(G)$ ratio increases above 0.05 J/cm^2 , and thus the amount of defects (Fig. 4.7c). The Tuinstra-Koenig relation [100] states that the $I(D)/I(G)$ ratio is proportional to $1/L_a$ with L_a the average grain size. Thus L_a on glass decreases with increasing fluence.

On Au, the ratio practically stays unchanged, even above the ablation threshold $F_{th,a} = 0.08 \text{ J/cm}^2$. Obviously, the thermal conductivity of the substrates plays an important role. Au serves as an efficient heat sink in contrast to glass, so that the grain sizes only is significantly affected by the increased local temperatures on glass caused by higher fluences, but

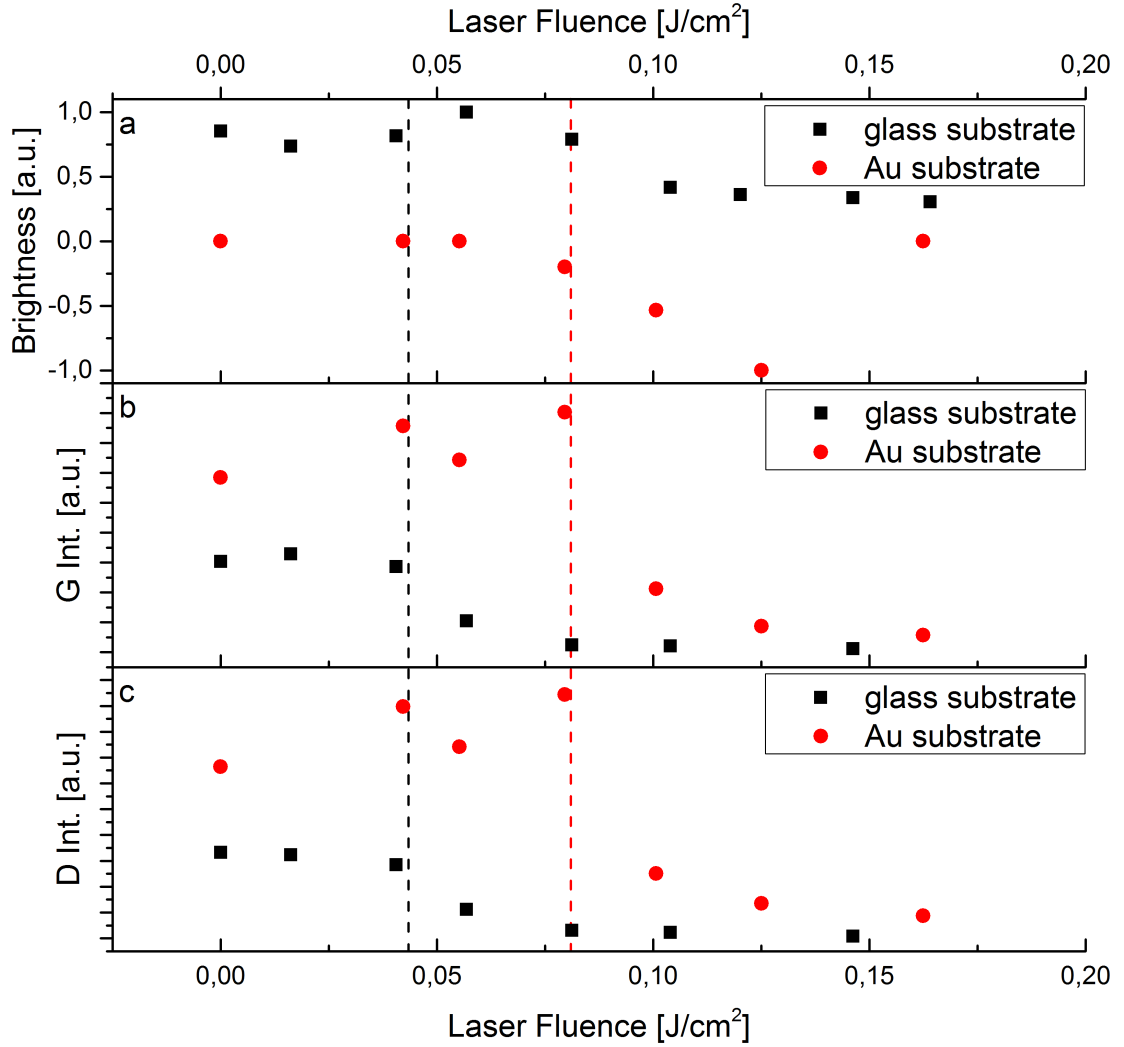


Figure 4.6: Results of the evaluation of microscopic images and Raman spectra concerning the ablation threshold of GO (marked as black dashed line for glass substrate and red dashed line for Au substrate). (a) Brightness of rGO areas under the optical microscope. (b) Absolute intensity G-band. (c) Absolute intensity D-band.

not on the good heat conductor Au.

The $I(2D)/I(G)$ ratio behaves analogously to $I(D)/I(G)$ (Fig. 4.7d). At a small number of pristine graphene layers (≤ 5) it was shown that by using the band shape of the 2D region it is possible to estimate the number of graphene layers [37]. The $I(2D)/I(G)$ ratio could be related to the ablation. On the other hand, the relative intensity of 2D peak may be also caused by the density of disorder [24]. The position of the D and G bands are not constant, but changes with the fluence (Fig. 4.7a and Fig. 4.7b). On glass, above 0.04 J/cm^2 , the D band shifts from 1344 cm^{-1} to 1352 cm^{-1} where grain sizes are reduced. Above 0.07 J/cm^2 , the position interestingly decreases again.

On Au, the D band position starts at a similar value of 1344 cm^{-1} as on glass, and increases

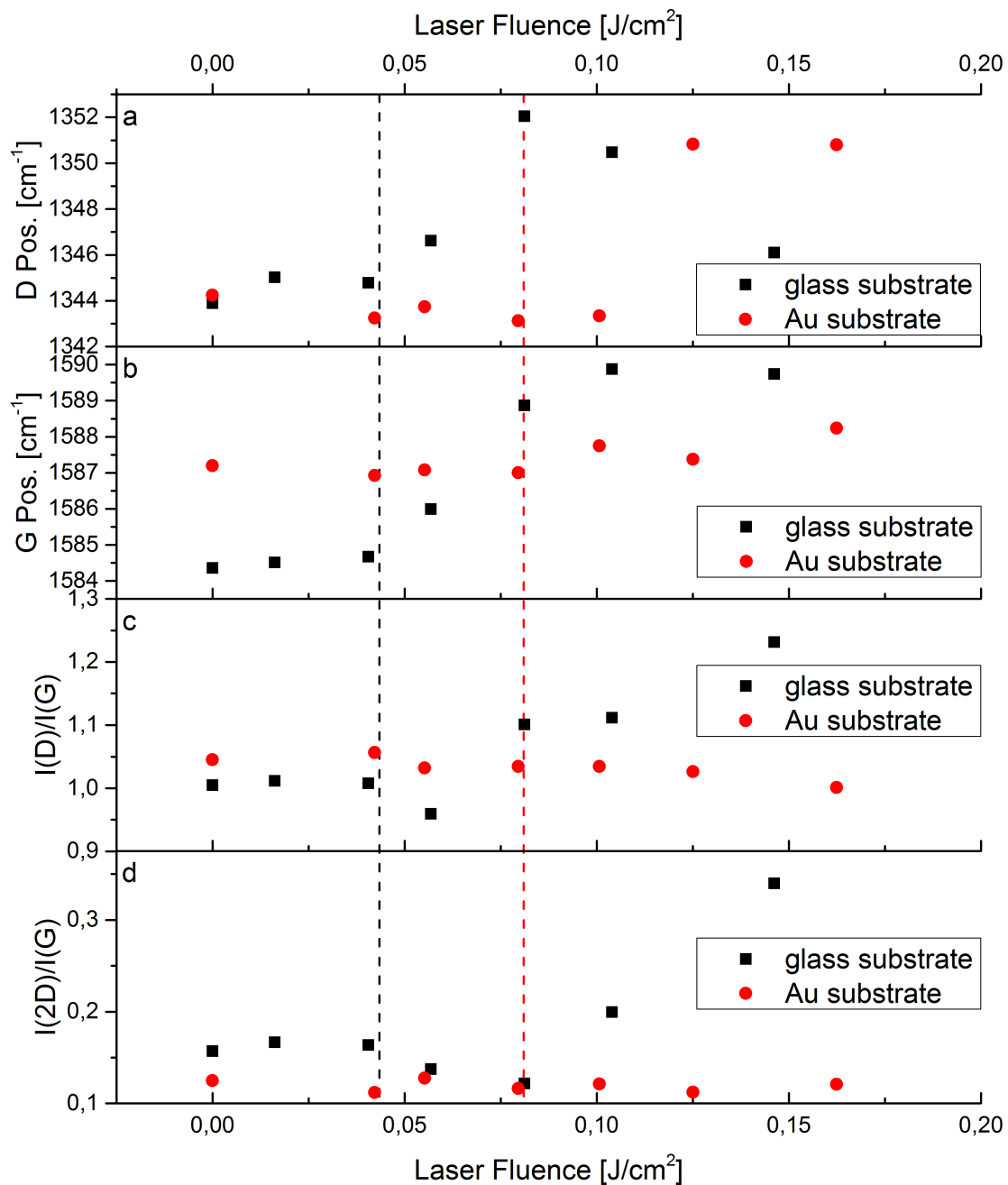


Figure 4.7: Results of the evaluation of Raman spectra concerning the defects. Ablation threshold of GO marked as black dashed line for glass substrate and red dashed line for Au substrate. (a) Position D-band. (b) Position G-band. (c) $I(D)/I(G)$ ratio. (d) $I(2D)/I(G)$ ratio.

to 1351 cm^{-1} , similar to glass, however above $0.10 \text{ J}/\text{cm}^2$. The G band position is related to sp^2 carbon. The positions on glass and Au show an analogous behaviour as the $I(D)/I(G)$ ratio (Fig. 4.7c) which is determined by the defect density. Obviously, the G band is affected by defects in this case.

4.3.3 Electrochemistry of the Reduced Areas

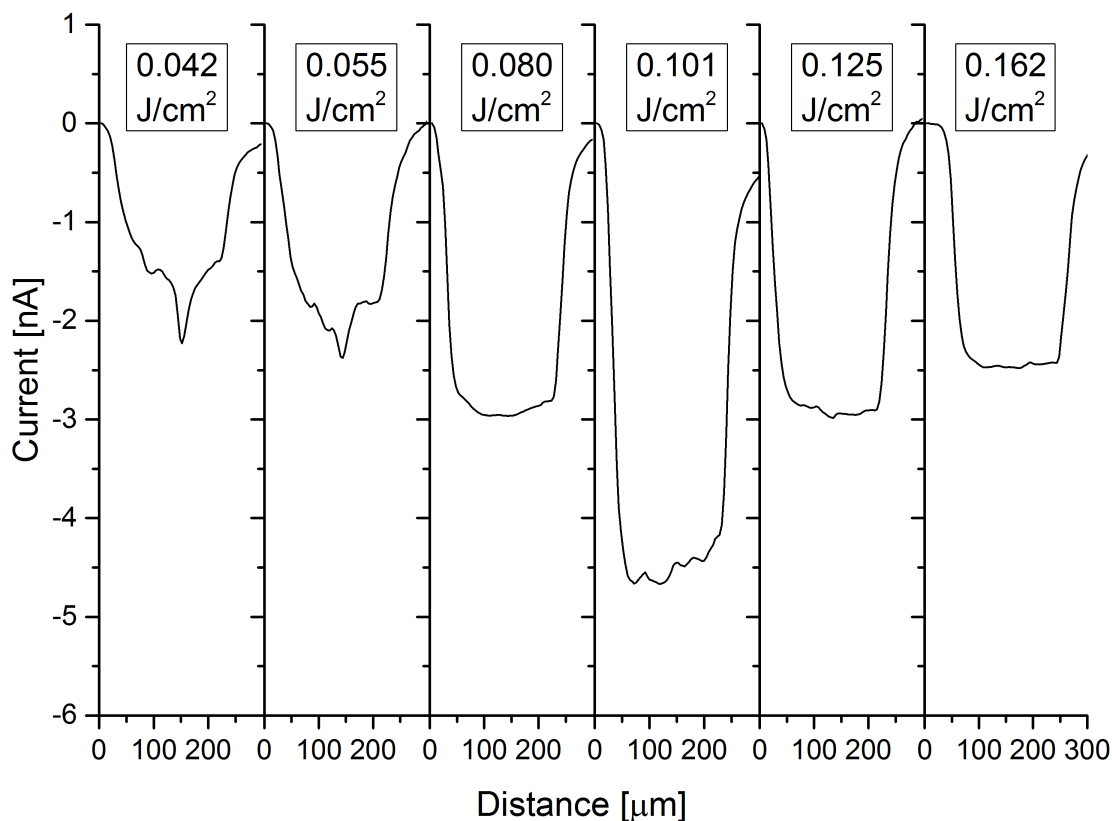


Figure 4.8: Scanning electrochemical microscope line scans over the laser reduced graphene oxide regions.

The conductivity (or rather the electrochemical activity) of the rGO patterns were investigated by a SECM. A microelectrode was scanned at constant distance over the sample surface and gave a positive feedback for conductive regions (i.e. rGO) and a negative feedback for insulating regions (i.e. GO). A more detailed description of the principles of this technique can be found in section 5.2.

Fig. 4.8 shows the results of line scans over the reduced areas on the Au substrate. This technique could only be performed on a conductive substrate such as Au, and not on glass. The first interesting observation is that at all fs-laser fluences the reduced areas give a positive feedback, i.e. show electrochemical activity. Obviously a reduction of GO took place. Only the current difference between the irradiated and the non-irradiated regions is presented. All rGO patterns show a positive feedback and are therefore conducting.

The feedback current differences vs. fluence (Fig. 4.9b) is compared to the reflectivity data

(Fig. 4.9a). The cathodic current increases at fluences up to 0.101 J/cm^2 due to increasing generation of conductive rGO. At higher fluences with increased ablation the current is reduced to a value characteristic of Au.

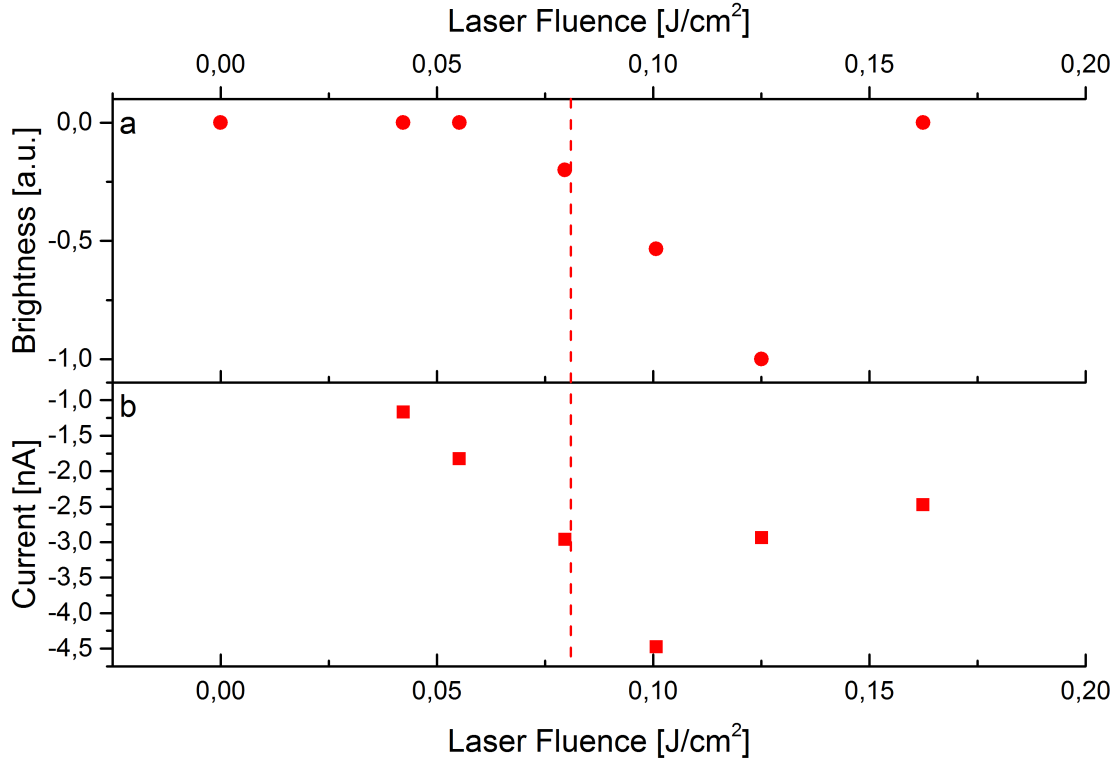


Figure 4.9: Evaluation of the SECM line scans (b) compared with the evaluation of the optical microscope images (a) on Au.

4.4 Conclusion

GO coatings were prepared via spincoating on glass and gold substrates. These coatings were reduced with a fs-laser at different fluences. The reduced areas were investigated via Raman spectroscopy. Ablation thresholds were evaluated for glass $F_{th,a} = 0.04 \text{ J/cm}^2$ and for Au $F_{th,a} = 0.08 \text{ J/cm}^2$. The ablation of GO on glass substrates happened at lower laser fluences than on Au. Keeping an at least partially photothermal mechanism in mind, the Au substrate could dissipate accumulated heat and desires therefore higher energies to reduce GO. The reduction of GO and the ablation overlap in a certain region. On gold a wider window for the laser fluence for the reduction of GO was found.

Raman spectroscopy enabled the interpretation of the generation of disorder in GO/rGO. At higher fluences, more defects were generated on glass. The grain size was decreased. On gold these effects were negligible small. The heat dissipation on gold seems to have a

positive effect for the final structure of the product.

An SECM was utilized for observing the influence of the used fs-laser fluence to the electrochemical activity. Also the patterns generated by the lowest fluences, which were neither visible via optical microscopy nor via Raman spectroscopy, showed significant electrochemical activity in comparison to the untreated GO areas. At appr. 0.08 J/cm^2 , i.e. in the same region as the changes of the Raman spectra occurred, an increasing electrochemical activity could be observed, which confirms that at these fluences structural changes must happen, which influence the material's electrochemical properties.

Chapter 5

Graphene Oxide Reduction with a Scanning Electrochemical Microscope

5.1 Introduction

The conventional electrochemical reduction of GO coatings is performed on conducting substrates, which work themselves as electrodes. They are coated with GO, immersed into an electrolyte and polarized cathodically [114]. However, there is also a method to reduce GO coatings on insulating substrates [114]. A thin tip works as electrode and is in direct mechanical contact to the GO coating on the insulating substrate. A cathodic polarization induces the electrochemical reduction of the GO, which is touched by the tip. In the next step, this just reduced rGO-region functions itself as an electrode, because rGO is electrically conducting in contrast to GO. This allows a lateral growth of an rGO-region.

A scanning electrochemical microscope (SECM) was used to image single GO flakes on a conducting substrate [86]. It was shown that the choice of the redoxactive species in the solution plays a crucial role. An SECM is an electrochemical imaging technique, which contains a movable microelectrode, which is connected to a bipotentiostat and can be scanned over a sample surface at controlled distances.

An SECM was also used to electrochemically "write" defined patterns into a GO coating [69]. However, the above described mechanism should have resulted in a growing rGO region, which was not observed. Therefore, some questions about the actual mechanism of the reported process remain.

In this work, an SECM was used to reduce defined spot arrays on a GO coating. It allowed to position the microelectrode precisely on the coating surface and to create reproducible conditions to investigate the growth mechanism of an rGO spot in a GO coating.

5.2 Scanning Electrochemical Microscopy

The scanning electrochemical microscope (SECM) is an electrochemical imaging technique [9, 94]. It belongs to the family of the scanning probe techniques. A small electrode with defined geometry, f.i. an ultramicroelectrode (UME), is scanned over the sample surface and can analyse the electrochemical behaviour of the sample locally.

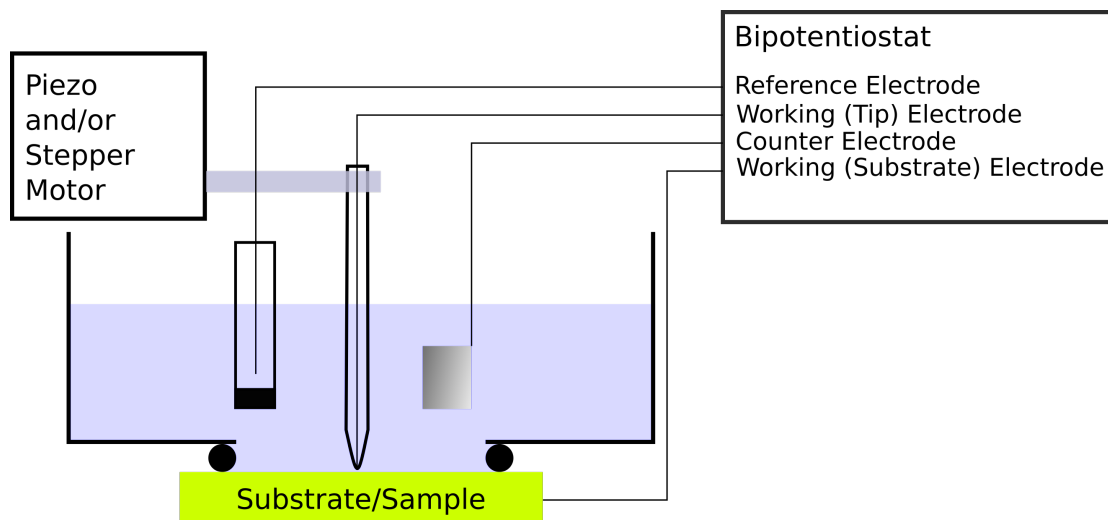


Figure 5.1: Scheme of a scanning electrochemical microscope.

An SECM basically consists of a bipotentiostat, a piezo-positioner, and the appropriate controlling system (Fig. 5.1) [94]. The typical electrochemical setup includes a bipotentiostat, a reference electrode, a counter electrode and two working electrodes. Two working electrodes are necessary, because the potentials of the substrate, which is usually the sample, and the UME must be controlled independently. The potential of the UME must be defined in every measurement, otherwise the SECM does not work. The control of the substrate potential is not necessary in every measurement. All the electrodes are located in an appropriate compartments.

The UME is mounted on an XYZ-stage. This enables the controlled approach of the UME to the substrate and the scanning of the substrate electrode in lines, squares, or other more sophisticated geometries [6]. This stage can be based on stepper motors, piezo motors, or the combination of both, depending on the required precision. With a conventional UME with an electrode-diameter of several micrometers, a stepper motor stage is sufficient.

The most crucial step in planning a SECM experiment is to choose a system, where the instrument yields appropriate feedback. There are many different kinds of feedbacks, which are described in literature. However, the possibilities are virtually endless and depend only on the scientist's creativity [6]. The two most important feedback mechanisms shall be presented here: the positive and the negative feedback (Fig. 5.2) [10, 12].

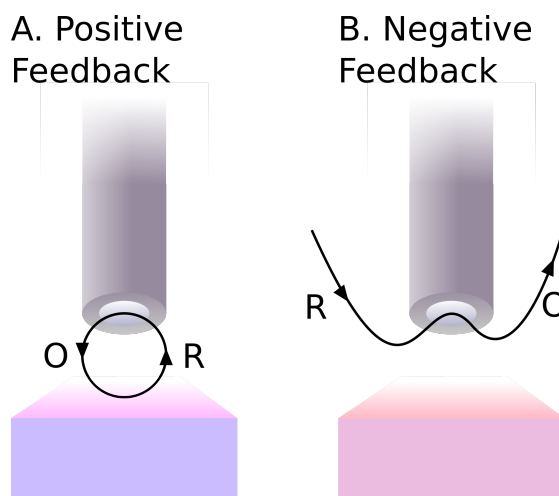


Figure 5.2: Positive (A) and negative (B) feedback mode in scanning electrochemical microscopy.

Let's assume a strong electrolyte containing additionally any redoxactive species, which exists in the solution as its reduced form R . The UME is far away from the substrate and its potential is constant and anodic of the redox potential of R . R will be oxidized to O . After an initial phase, a diffusion limited constant current will establish on the UME.

When the UME is positioned at distances comparable to the diameter of the UME, i.e. a few micrometres, case 1 of the positive feedback takes place (Fig.5.2A): the substrate is a conductor and polarized cathodic to the redox potential of the redox active species. A redox cycle will evolve, where the redoxactive species is oxidized at the UME and reduced at the substrate. This is faster than the diffusion of R to and O from the UME. Therefore the measured current will increase with an UME approach.

The second case is the negative feedback (Fig.5.2B). The substrate is an insulator and does not rereduce the redox active species and the mass transport of R to the UME is hindered. Thus, the current on the UME will decrease.

5.3 Experimental

GO was spin coated onto conventional microscope glass slides. The procedure is reported in chapter 2. Four coating steps were applied. Thus, the final layer thickness was approximately 12 nm.

A commercial SECM instrument (CHI920D) was used. A custom cell was designed and

produced by a 3D printer (Ultimaker B.V.; model Ultimaker²) out of acrylonitrile butadiene styrene. As electrolyte served a 1 *mM* FcMeOH and 100 *mM* KNO₃ aqueous solution.

The microelectrode with a diameter of 25 μm was approached to the surface controlled by a negative current feedback in order to avoid damage of the tip and the substrate. GO spots were reduced at a constant potential of -0.89 V vs. SHE and different reduction times. An rGO spot started growing originating at the tip position. Fig. 5.3 shows microscopic pictures of a growing rGO spot recorded with a Dinolite microcamera.

The characterization of the samples was carried out with a WITec alpha 300A Raman microscope. The excitation wavelength was 532 nm with a laser power of 0.1 mW.

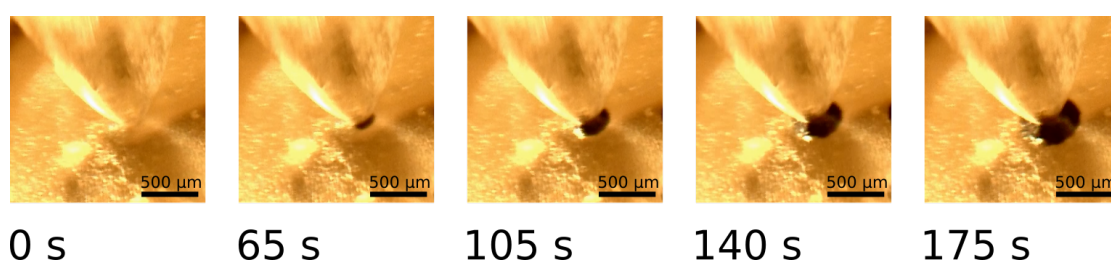


Figure 5.3: A reduced graphene oxide spot grows in the graphene oxide coating.

5.4 Results and Discussion

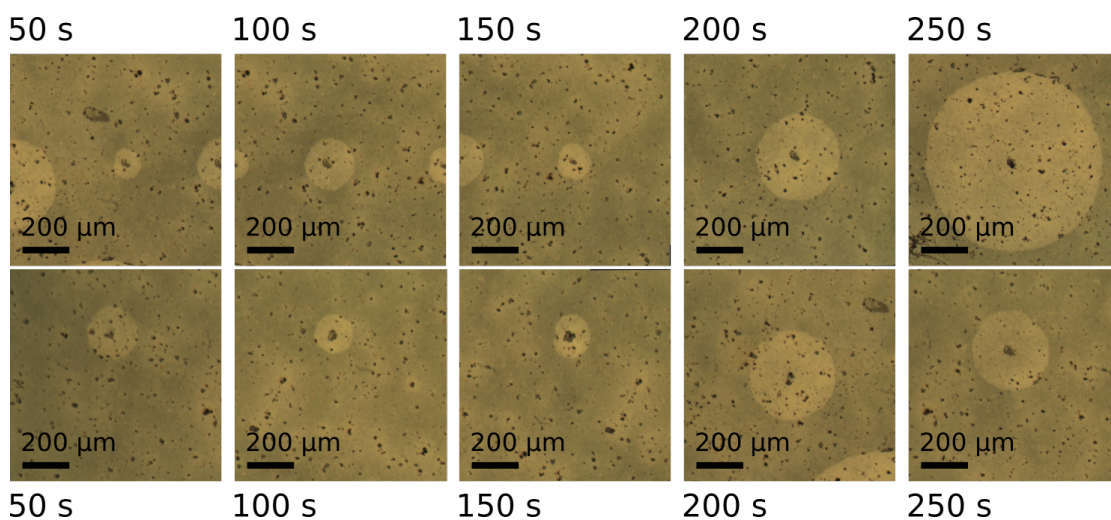


Figure 5.4: Reduction spots generated with an SECM at different reduction times, corresponding to the first and second row. Each reduction was performed twice on independent positions.

Fig. 5.4 shows microscopic images of rGO spots generated by an SECM. They were generated at constant potential and different reduction times between 50 s and 250 s. Each

reduction was performed twice, corresponding to the first and second row in the picture. From these microscopic images it is evident that there is not a clear relationship between the reduction time and the spot area. Higher reduction times seem to produce increasing spots, however, with no linear relationship. This means that the growing rate is not constant during various experiments. This phenomenon may depend on the quality of the respective contact of the UME to the GO coating. The better the contact, the faster the rGO spot grows. Actually, it has to be expected that the consumed charge and the spot area exhibit a linear correlation according to the Faraday's law. This could be confirmed experimentally (Fig. 5.5). The consumed charge is proportional to the amount of reduced groups, which itself is proportional to the reduced area (under the assumption the these groups are homogeneously spread and the coating thickness is constant over the observed area).

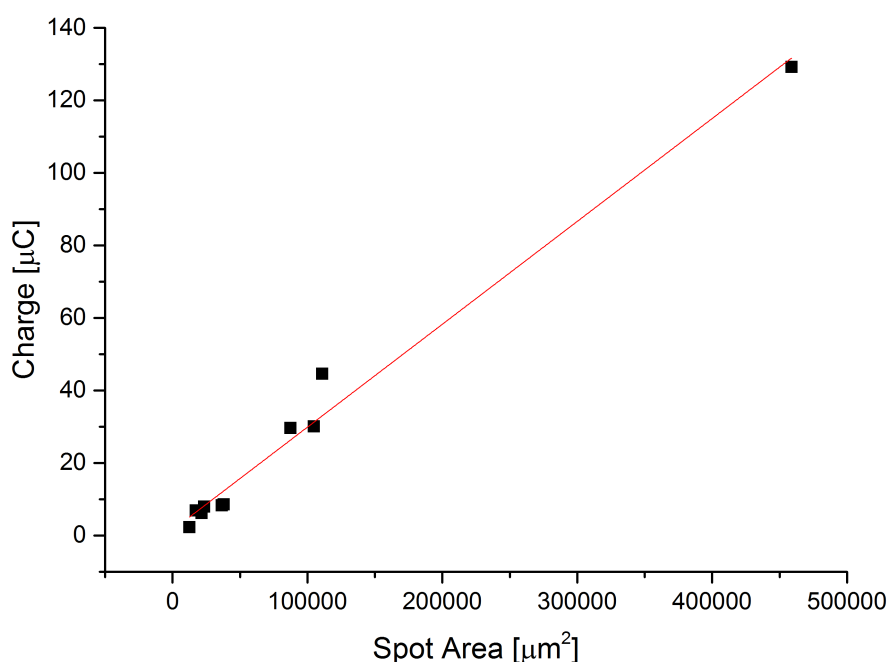


Figure 5.5: Consumed charge during the SECM reduction vs. area of rGO spots

Charge and current behaviour over time is plotted in Fig. 5.6. The spot area, and thus the charge, show a quadratic relationship to the elapsed reduction time. This demonstrates that the radius of the rGO spots grow at constant speed which can be seen in Fig. 5.6 (upper graph).

The working electrode, i.e. the interface where the reaction of interest occurs, is initially the microelectrode tip. After further GO reduction, it is the circular interface between the rGO region and the surrounding GO phase. In general, it is the circle around the spot and for this considerations it can therefore be regarded as a one dimensional electrode. This interface

is proportional to the radius (which is growing at constant speed). Generally the current in an electrochemical experiment is proportional to the electrode area. Thus, the current should be linearly dependent on the elapsed reduction time because it is proportional to the circumference of the rGO region. This was confirmed by the experiment (Fig. 5.6, lower graph).

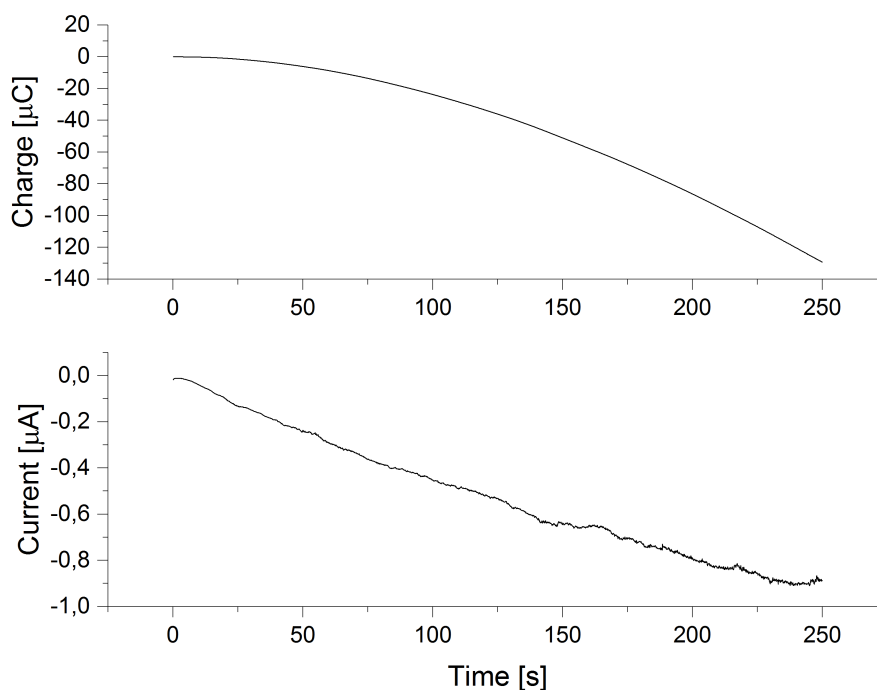


Figure 5.6: Consumed charge and current during the SECM reduction process.

Raman spectroscopy was performed to investigate chemical changes in the material during the reduction process. Fig. 5.7 shows false colour images of an rGO spot, based on four different important values and ratios. During the reduction process, the D and the G bands shift significantly (Fig. 5.7a,b). The D band (Fig. 5.7a) of GO is located at appr. 1345 cm^{-1} . After the reduction it is shifted to appr. 1340 cm^{-1} . The G band shifted to higher wavenumbers during the reduction process, from appr. 1580 cm^{-1} to appr. $1585 - 1590\text{ cm}^{-1}$ (Fig. 5.7b). Fig. 5.7c shows a false colour image for the $I(D)/I(G)$ ratio. It rises during the reduction process, which means that the density of disorder is increasing. These results are analogous to those of the fs-laser reduction, shown in chapter 4. The $I(D)/I(G)$ ratio is an important value for characterizing carbon materials. It provides information about the amount of disorder in the carbonaceous species and is proportional to $1/L_a$, where L_a is the average crystal size. Thus L_a decreases during the reduction [100]. The G-band originates from in-plane sp_2 vibrations and the D band bases on the excitation of a charge carrier,

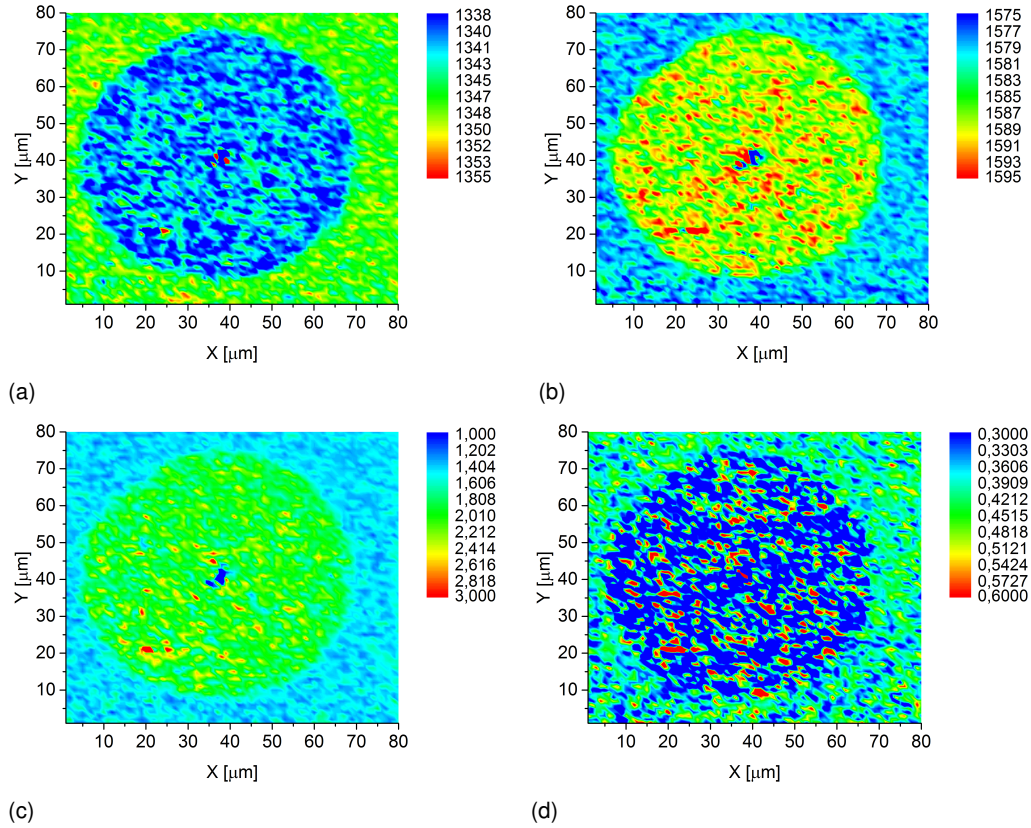


Figure 5.7: Results of the evaluation of the Raman spectra of a rGO spot. (a) Position of the D band. (b) Position of the G band. (c) $I(D)/I(G)$ ratio. (d) $I(2D)/I(G)$ ratio.

which is inelastically scattered by a phonon, followed by a second elastic scattering by a zone boundary or defect [24]. Fig. 5.7d represents the $I(2D)/I(G)$ ratio which increases during the reduction. Furthermore, it can be seen, that this ratio is not homogeneous in the reduced spot, but varies over a wide range.

A True-Component-Analysis was applied to the Raman spectra. In this approach, a mix of spectra is separated into the components and their weightings. Two components were found, corresponding to GO and rGO (Fig. 5.8). The colour map in shows the distribution of these. Blue areas correspond to rGO, red areas correspond to GO. Actually, the majority in the reduced spot is related to rGO. The red and blue spectra in Fig. 5.8 represent GO and rGO, respectively. They show mainly the same results as in the peak fit analysis. The position of the D band decreases from 1347 cm^{-1} to 1341 cm^{-1} during the reduction, whereas the position of the G band increases from 1582 cm^{-1} to 1591 cm^{-1} . The $I(D)/I(G)$ ratio increases during the reduction from 1.1 to 1.4, which means that the amount of defects in the structure increases. The $I(2D)/I(G)$ ratio decreases from 0.12 to 0.09

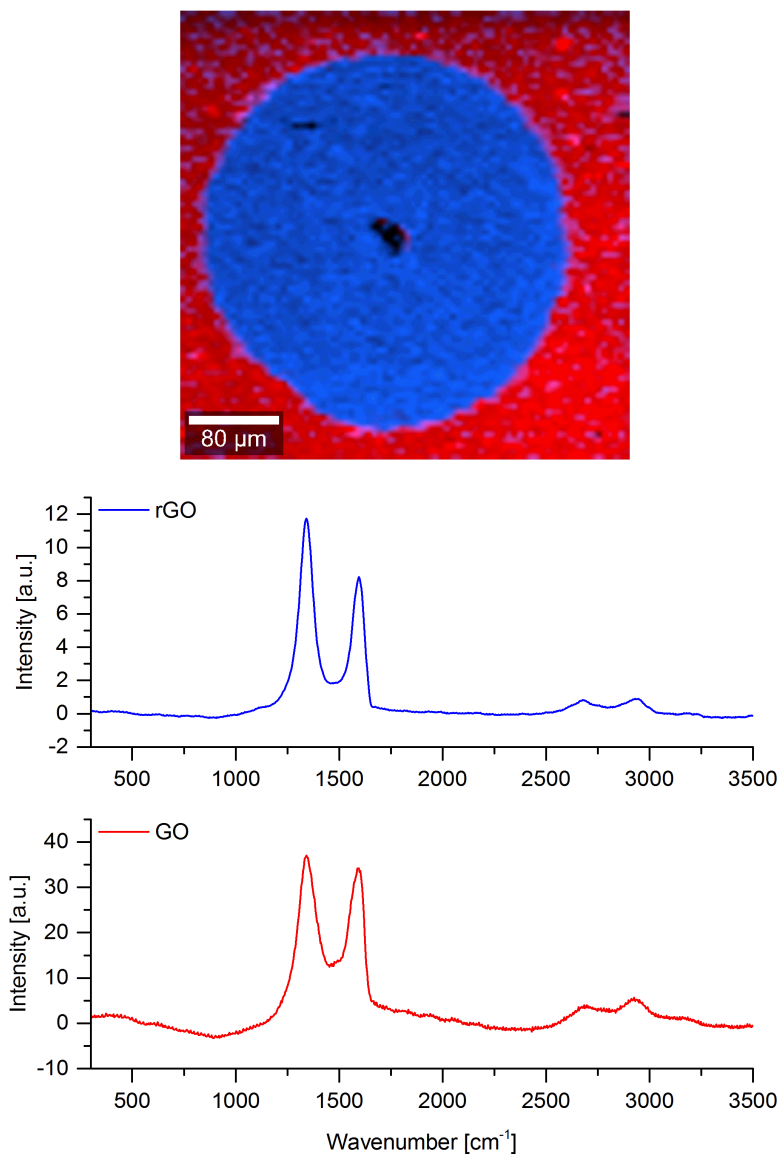


Figure 5.8: Results of the true components analysis. Blue: reduced graphene oxide. Red: graphene oxide

5.5 Conclusion

The tip of an SECM was used to reduce GO coatings locally. In this process, the already reduced part of the GO coating functions as working electrode. Thus, the GO coating is reduced at a growing circumference of the rGO spot.

The rGO spots were prepared with different reduction times. No clear correlation was found between the reduction time and the final size of the spots. This can be understood by a variable mechanical contact of the microelectrode tip to the coating. Therefore the growing speed varies between the spots and spot size cannot be controlled by the reduction time.

However, a direct, linear correlation was found between the spot area and the consumed charge. Thus, the charge can be used as parameter for the generation of rGO spots of a certain diameter.

During the reduction process, the radius of the rGO spots is propagating at constant speed. The current is proportional to the circumference of the spot and is therefore increasing linearly during the reduction. The charge, on the other hand, is proportional to the spot area and is growing quadratically.

The rGO spots were characterized via Raman spectroscopy. A peak fit analysis and a true components analysis showed that the positions and the intensity ratio of the D and G bands change during the reduction process. The amount of defects in the structure increases.

Chapter 6

Beyond the Mechanism of the Graphene Oxide Reduction: A Spectroelectrochemical Study

6.1 Introduction

In this section the electrochemical reduction mechanism shall be elucidated. The reduction mechanism and the structure of the final product are of great interest, because they affect the final properties of the material. Thus, the degree of oxidation of the starting material [32] plays an as important role as the reduction parameters [98].

There are just few publications concerning the reduction mechanism of GO. *In-situ* measurements in organic solvents [102] showed the relevance of C=O, O–H and C=C bonds. However, the more important reduction medium is water, which is used in numerous proposed applications. Measurements were performed in H₂O [103] where the reduction of several oxygen containing groups in a narrow potential range was described. This seems counter-intuitive, because due to the diverse chemical structure of GO a multi-step electrochemical reduction mechanism must be assumed.

This work allowed to clarify this mechanism via the technique of an *in-situ* attenuated total reflection FTIR (*in-situ* ATR-FTIR) spectroscopy investigation. The transformation of oxygen containing groups in GO was monitored. Measurements in D₂O solutions provided insight into the role of protic and aprotic groups. The multivariate curve resolution - alternating least squares (MCR-ALS) method was used for evaluating spectroscopic data [29, 52, 53].

6.2 Spectroelectrochemistry

Spectroelectrochemistry is an extremely powerful tool for understanding electrochemical mechanisms on a molecular level. As an *in-situ* technique it is the concurrent combination of a spectroscopic analysis with an electrochemical experiment [11]. There are spectroelectrochemical instrumentations over wide wavelength regions [57], but in this study we want to focus on FTIR-spectroelectrochemistry [13, 51], which is most useful for following and understanding structural changes on the molecular scale.

When setting up a spectroelectrochemical experiment - especially FTIR - one will soon realize that the combination of an electrochemical experiment with molecular spectroscopy is a challenging compromise [13]. Virtually all common solvents in electrochemistry are strong IR absorbers and will not let an IR beam pass through them. Thus, the most difficult task will be to guide the IR-beam to the electrode surface, where the reaction of interest occurs. The solution for this is a sophisticated cell design [13]. In FTIR spectroelectrochemistry,

there are basically two practised approaches to solve this problem: the external reflection geometry and the internal reflection geometry.

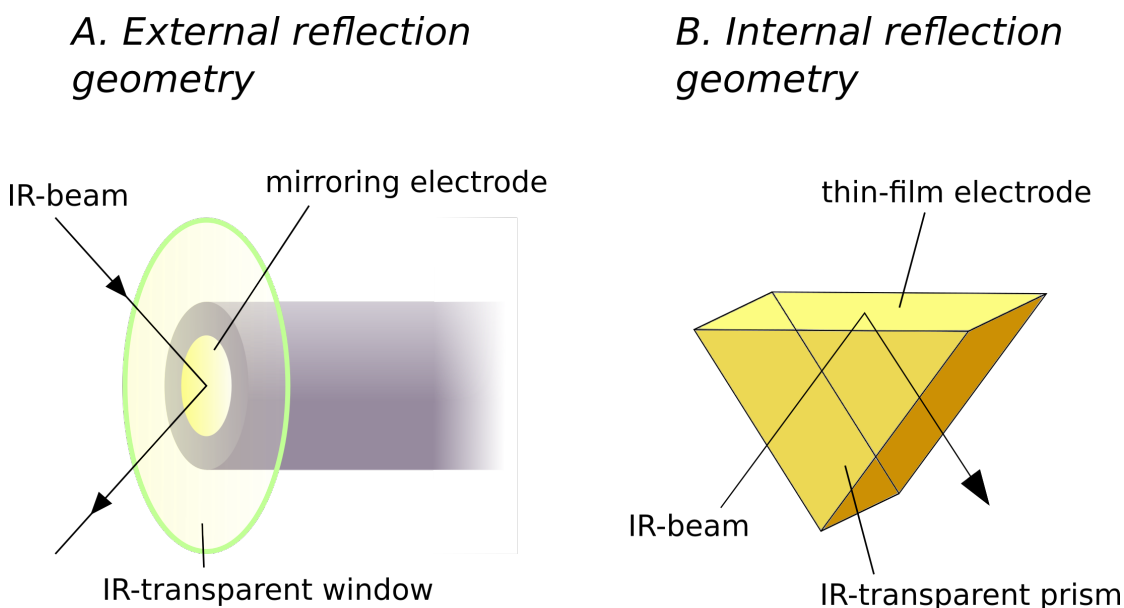


Figure 6.1: Sketch of the external reflection geometry (A) and internal reflection geometry (B) in IR-spectroelectrochemistry.

In the external reflection setup, the IR-beam is reflected on a polished electrode surface [110]. The compromise to the above mentioned problem, that the solvent is a strong IR absorber itself, is to position the electrode in close proximity to an IR transparent window (Fig. 6.1A). Thus, the distance the IR-beam passes through the electrolyte is minimized, usually a few micrometres. Sufficient light will reach the detector to obtain a spectrum.

The main problem of this approach is that diffusion will be severely hindered to and from the electrode by this thin gap. The solution to deal with this problem is to mount the working electrode on a micrometer head [110]. Then, the distance between the electrode and the gap can be increased when changing the potential, and diffusion can occur. When recording a spectrum, the electrode is moved again close to the window. So it will be possible to obtain satisfying spectra. Although, the potential-current curves are hard to be interpreted due to the repetitive motion of the electrode and the resulting mixture of the solution. Therefore, a comparison with a conventional electrochemical setup will be necessary.

The internal reflection geometry (Fig. 6.1B) bases on the phenomenon of the attenuated total reflection [59]. If light passes from an optically denser medium into an optically less dense medium - like f.i. from silicon to water - and the angle of incidence is exceeding the

so-called Brewster angle, then the light is completely reflected.

On the spot, where the light is reflected, an evanescent field establishes. Light is penetrating into the optically less dense medium and can be partially absorbed there. The depth of penetration depends on the wavelength and is about half the wavelength [74]. The light decays exponentially with the distance to the denser medium, which means that this technique is most sensitive directly on the interfaces and is therefore applicable for analysing the Helmholtz layer.

The challenge of this technique is to apply a working electrode on the ATR prism. One solution is that the prism is a conductor itself. There are some materials like f.i. doped Si, which are IR transparent and electrically conducting [11, 57]. Or, a thin film electrode must be applied on the prism surface. Usually Au layers of a few nanometres are sputtered onto the prism [62]. There are two challenges. Firstly, the prism must be covered completely. If parts of the prism are in contact with the electrolyte, this can be a problem, especially if the prism material is itself electrochemically active. Secondly, the thin film electrode must be stable itself. It must not dissolve or delaminate during the electrochemical experiment.

6.3 Multivariate Curve Regression - Alternating Least Squares (MCR-ALS)

Multivariate Curve Regression - Alternating Least Squares (MCR-ALS) was initially used in chemometrics. It can be applied for the separation of multiple-component systems [53]. The usual routine for evaluating spectroelectrochemical experiments would be to integrate certain bands and follow their course in dependence of the potential. Then, these bands may be recombined to spectra of the expected products and intermediates. This offers a wide scope of interpretations and can lead to misunderstanding.

In MCR-ALS one tries to optimize a set of parameters, which is usually easily adaptable to the investigated system. Initial estimates, like the number of involved components, are required. Finally the technique results in the spectra and concentration variations of all participating molecules.

The basic model of this method is represented in Eq. 6.1. The idea is that the resulting perturbed spectra can be obtained by a matrix multiplication of a matrix containing the pure components' spectra and a matrix containing the concentration profiles of these.

$$D = C \cdot S^T + E \quad (6.1)$$

In this equation D ($M \times N$) is the obtained experimental spectra matrix, M is the number of spectra, N the number of data points per spectrum, and F the number of pure components. C ($M \times F$) is the matrix of the concentration profiles. S^T ($F \times N$) represents the spectral matrix of the pure components and E is the residuals matrix with no further physical meaning [52, 53]. Fig 6.2 shows a schematic representation of this equation with an example of three components.

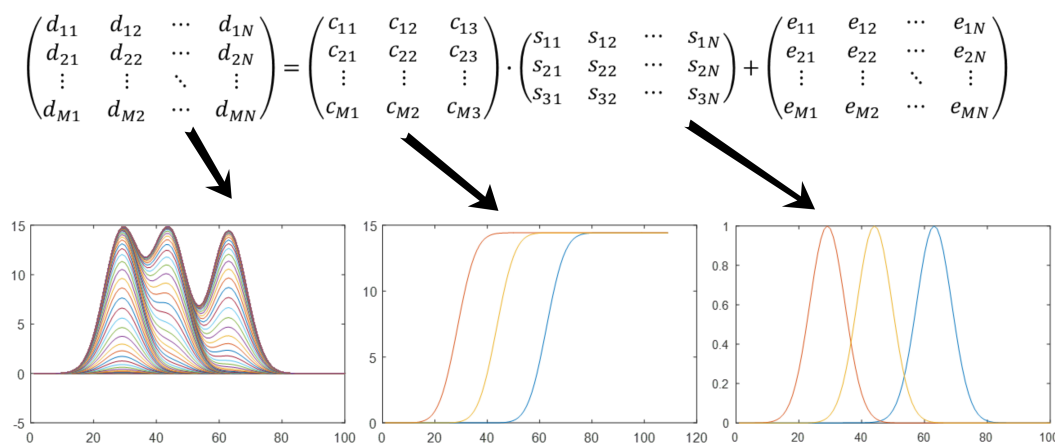


Figure 6.2: Scheme of the underlying model of Multivariate Curve Regression based on a three component system.

C and S^T shall be obtained from D by optimization. For this, F must be set initially. Various methods can help to find a good estimate: singular value decomposition, evolving factor analysis, or principal component analysis. Certain constraints - like nonnegativity or unimodality - are vital for the iterative process of ALS (alternating least squares).

6.4 Experimental

6.4.1 Electrode design on the ATR-prism and *In-situ* Spectroelectrochemical Procedures

The detailed experimental is described the publication *In Situ FTIR and in Situ QMB Study of the Electrochemistry of Graphene Oxide on Platinum* [83], which is attached in Appendix B.

In short:

An *in-situ* electrochemical single reflection ATR cell was designed and produced by a 3D printer on the basis of acrylonitrile butadiene styrene (Fig. 6.3).

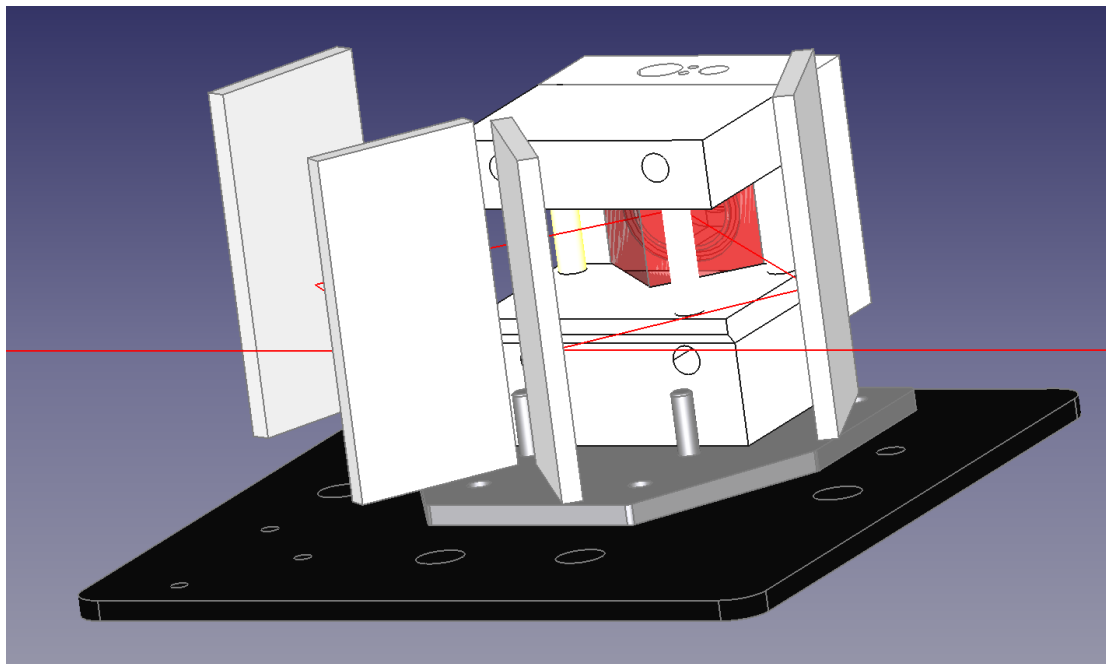


Figure 6.3: Spectroelectrochemical ATR measurement cell

For the electrochemical experiments, a conventional potentiostated three electrode setup with a platinum wire counter electrode and an Ag/AgCl reference electrode was used.

The working electrode was optimized to increase the spectroscopic sensitivity. A special Au pattern was evaporated onto the ZnSe ATR crystal. A thin film grid was connected to the potentiostat as working electrode (compare Fig. 6.1). The ATR detection region was located on the uncoated area. Only here electrochemically induced infra-red-active changes could be registered.

GO was spin coated onto the ATR prism. The procedure is reported in section 2. Four coating steps were applied. Thus, the final layer thickness was approximately 12 nm.

The so-prepared crystal was used in the spectroelectrochemical cell, where FTIR spectra were recorded during cycling voltammetry.

6.4.2 Peak fit routine

The spectra were fitted by a peak fit routine based on a commercial software (OPUS, Bruker Corporation) using a Levenberg-Marquardt algorithm. The following parameters were applied:

Table 6.1: Parameters for the peak fit routine

Position [cm^{-1}]	Width [cm^{-1}]	Position [cm^{-1}]	Width [cm^{-1}]
1097.4	63.1	1641.9	57.5
1205.8	55.0	2366.4	135.7
1327.1	35.4	2479.7	150.3
1366.9	32.3	2611.4	144.4
1425.6	33.8	2782.1	28.5
1458.9	31.7	2863.7	40.4
1500.9	31.6	2925.5	41.6
1552.1	37.1		

6.4.3 Multivariate Curve Regression - Alternating Least Squares (MCR-ALS)

The MCR-ALS analysis was performed in MATLAB R2015a (MathWorks) with a tool optimized for this environment [52]. The detailed description of the used parameter can be obtained from the publication *A Multivariate Curve Resolution evaluation of an in-situ ATR-FTIR spectroscopy investigation of the electrochemical reduction of graphene oxide* [83] attached in appendix B.

6.5 Results and Discussion

6.5.1 Cyclic Voltammetry

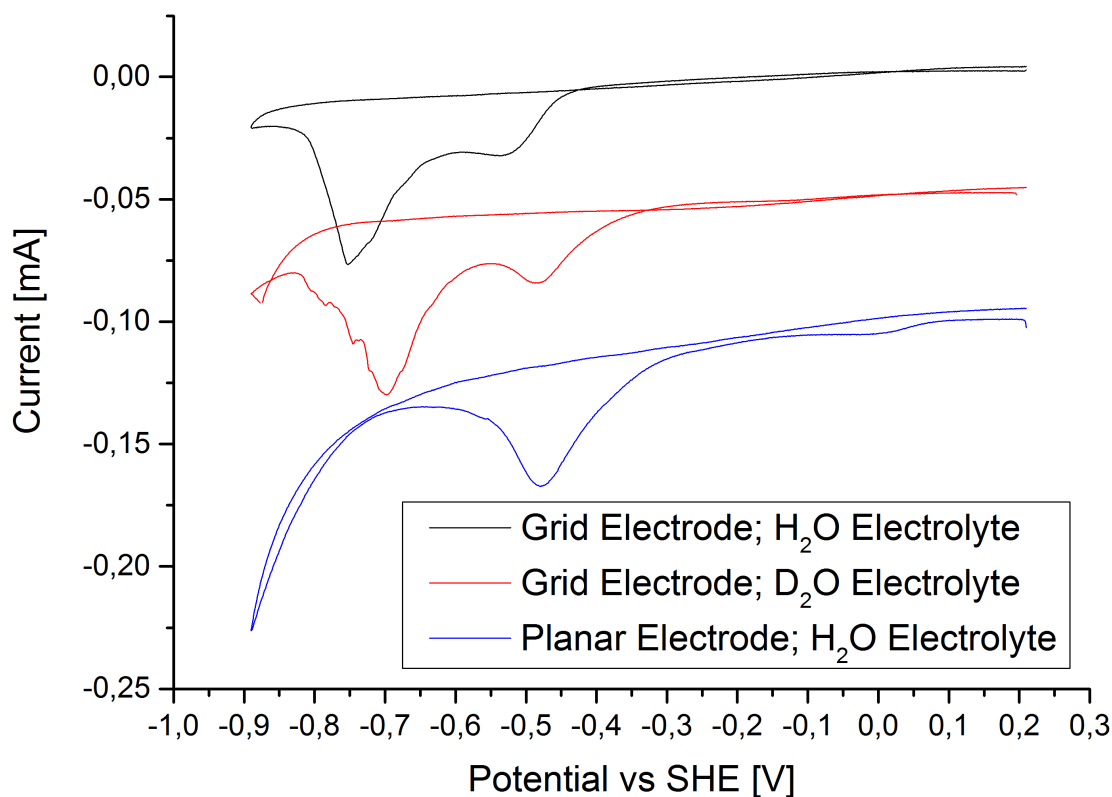


Figure 6.4: Cyclic voltammetry results of the electrochemical GO reduction

The cyclic voltammetry results of GO in D_2O and H_2O solutions (Fig. 6.4) show two reduction waves at $-0,5$ V and $-0,7$ V during the first reduction potential scan (black and red curves), when the experiments were performed on the Au grid. The planar electrode design delivered different results (blue curve).

GO reduction takes place at two different rGO regions (Fig. 6.5): one directly on the Au electrode surfaces, and one between the grid fingers on the insulating ZnSe surface. They caused two different overpotentials at $-0,5$ V for the Au surface and $-0,7$ V for the ZnSe surface. RGO regions, which are grown directly on the Au grid fingers exhibit lower series resistance and thus lower overpotential than on ZnSe.

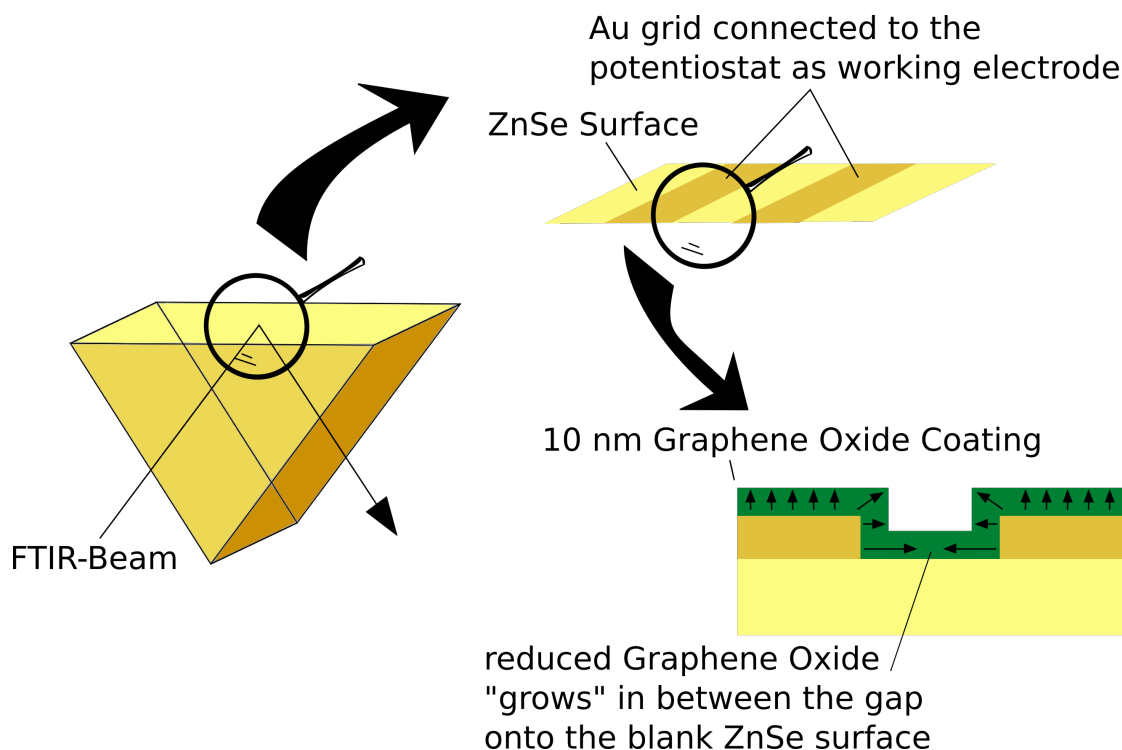


Figure 6.5: Sketch of the different areas on the ZnSe surface, relevant for the GO reduction.

For this study the peak at -0.7 V is of importance. The reduction takes place directly on the ZnSe surface and is therefore detectable via FTIR spectroscopy. A closer look shows that it consists of several peaks and indicates thus a multistep mechanism.

These findings can be compared with an analogous experiment on planar Au (Fig. 6.4 blue curve). In this case, only one reduction peak can be observed (i.e. the one at lower overpotentials, corresponding to the GO directly on the Au grid). The reduction peak originating from the grid structure vanishes. The GO reduction was reported in literature at comparable overpotentials [103].

This electrode structure on the ATR crystal must be taken into account for the interpretation of spectroelectrochemical measurements: Au-surface-rGO cannot be detected via FTIR spectroscopy, because it is concealed by the electrode fingers. On the ZnSe surface, rGO grows laterally between the Au fingers horizontally on the ZnSe surface, and can thus be detected by the spectrometer (compare Fig. 6.5). Therefore, only the peak at -0.7 V is discussed in this work.

This assumption can be confirmed by the FTIR evaluation, where only the reduction at -0.7 V shows significant changes in the spectra. At -0.5 V no spectral features were observed.

6.5.2 *In-situ* ATR-FTIR Measurements in H₂O

Fig. 6.6 shows the spectroscopic results of the reduction of GO in H₂O. Positive bands may be interpreted as the evolution, and negative bands as the consumption of a corresponding analyte.

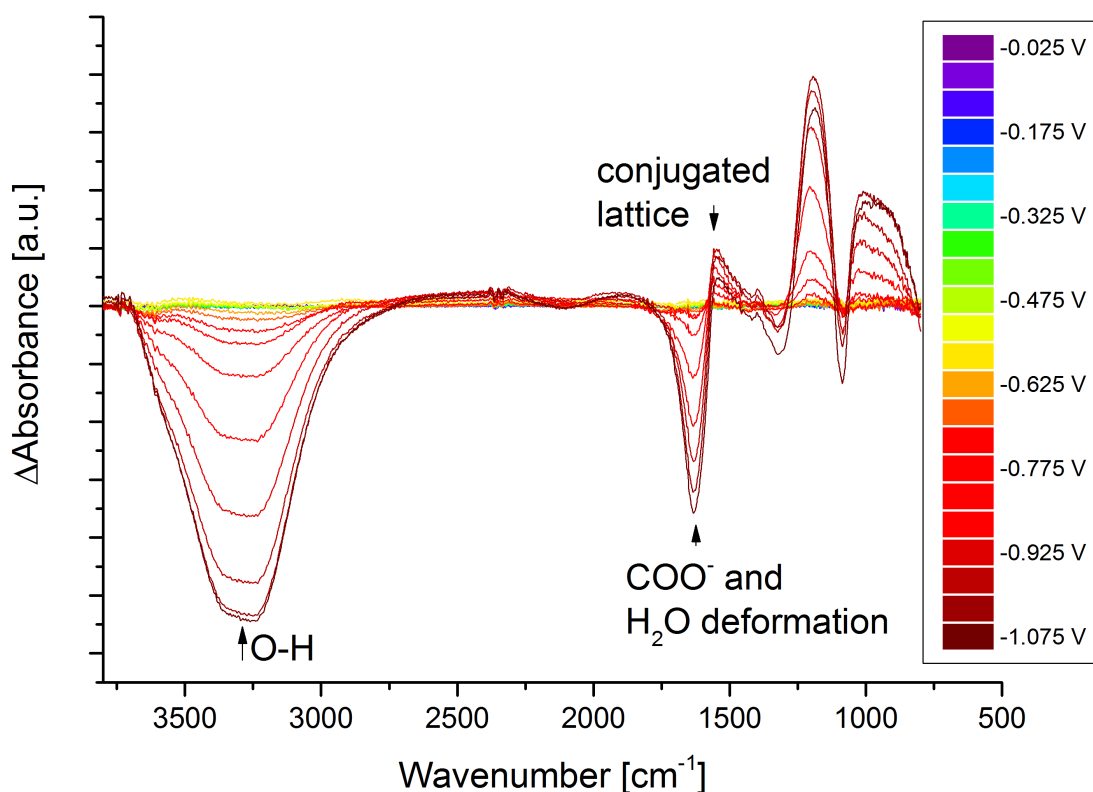


Figure 6.6: Spectroscopic results of the electrochemical reduction of graphene oxide in H₂O. The COO⁻ feature is assigned to graphene oxide, the conjugated lattice to reduced graphene oxide.

At 1640 cm⁻¹ a negative band represents the COO⁻ groups of the GO, and their reduction. The generation rGO is also traceable via the evolution of a conjugated lattice corresponding to the band at 1552 cm⁻¹.

In the O–H stretch vibration region between 3000 cm⁻¹ and 3500 cm⁻¹ a broad, intensive band shows the reduction of O–H bonds in different groups on GO. In this context, it must be considered that the solvent water absorbs in this region as well. The penetration depth of the evanescent field is dependent on the refractive indices of the electrolyte, ZnSe and interfacial species such as GO and rGO [34]. Consequently, the peak area of the measured water bands changes.

The bands of the GO and rGO coatings are not affected, because the coating is much

thinner than the extent of the evanescent field and is thus always completely penetrated by IR radiation. Regions between 3000 cm^{-1} and 3500 cm^{-1} (O–H) and at 1640 cm^{-1} (COO[−] and deformation vibration of water) are affected by this consideration. This results in the consequence that the quantitative interpretation at this crucial wavenumber region in H₂O is difficult.

6.5.3 *In-situ* ATR-FTIR Measurements in D₂O

In comparison to the H₂O data (section 6.5.2) the results of the measurements in D₂O show a clearer view of the GO reduction (Fig. 6.7).

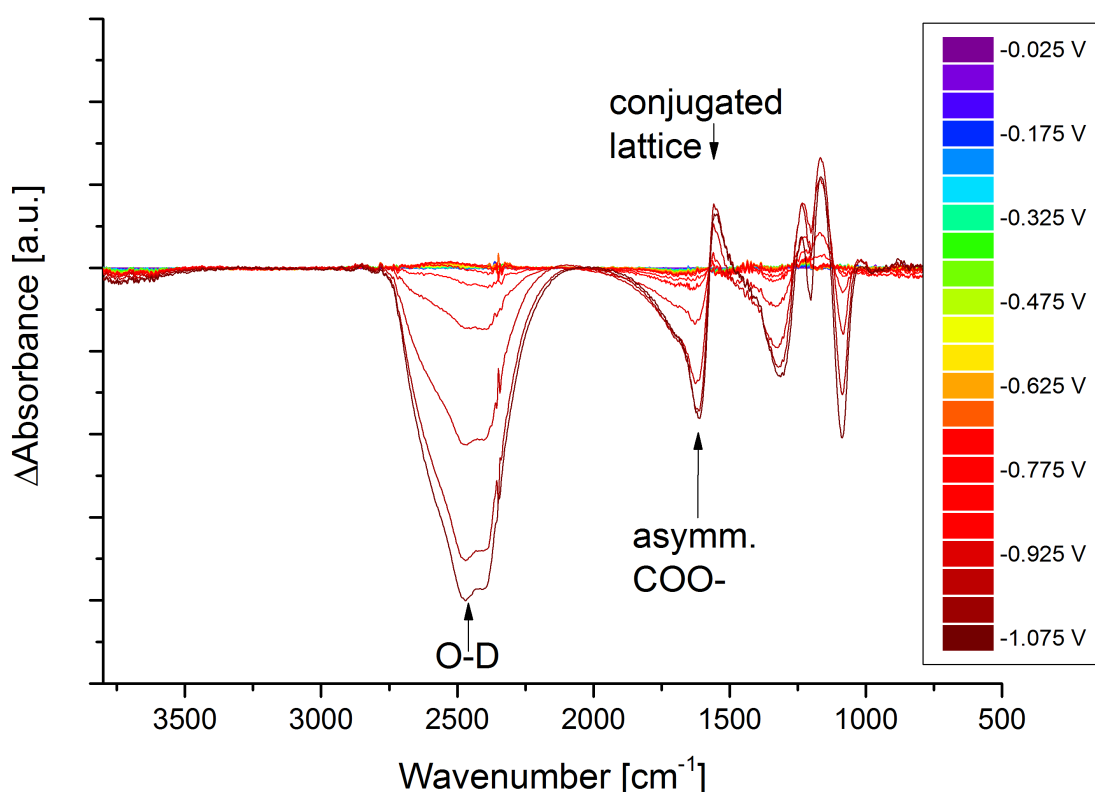


Figure 6.7: Spectroscopic results of the electrochemical reduction of graphene oxide in D₂O. The COO[−] feature is assigned to graphene oxide, the conjugated lattice to reduced graphene oxide. The bands of protic groups are shifted to lower wavenumbers in comparison to H₂O.

Because of the huge excess of the heavier deuterium in comparison to hydrogen, hydrogen is immediately exchanged by deuterium in any protic groups, because of the dissociation equilibrium. The remaining concentration of hydrogen can be neglected. The presence of deuterium shifts the bands of the deuterated groups to lower wavenumbers (see Tab. 6.2).

Table 6.2: Shift of the vibration bands in water and heavy water [91]

Indication	Water	Deuterated Water
$\nu_{a.s.,s}$	3000 – 3500 cm^{-1}	2200 – 2700 cm^{-1}
δ	1500 – 1800 cm^{-1}	1100 – 1400 cm^{-1}

Thus, all bands, which were not shifted due to the use of D_2O , were identified as aprotic groups.

Due to deuterium, the water deformation vibration shifts from 1640 cm^{-1} to lower wavenumbers. As a result, it is not overlapping the spectral features of GO in this region. An intensive band at appr. 1600 cm^{-1} is now visible and can be assigned to carboxylate groups.

Previous literature [43, 102] reported a C=O vibration at wavenumbers around 1750 cm^{-1} . The spectra in this work show a very small feature in this region, whereas the band at 1600 cm^{-1} is more intensive. The experiments were performed under aqueous conditions. Thus, the measured peaks of the carboxylate group are the symmetric and asymmetric COO^- stretch vibrations [61, 72] - and not the C=O stretch vibration.

This interpretation of the data presumes that carboxylate groups exist in their deprotonated form. The zeta [44] potential of GO sheets is appr. -35 mV for a pH higher than 4. Below pH 4 it rises significantly up to -15 mV. At this pH, carboxylate groups are deprotonated. Their protonation and the zeta potential are strongly correlated.

In this work, Na_2SO_4 solutions (pH 6-7) were used. Although they were unbuffered, a cathodic polarization can only result in increasing the local pH due to the possible electrolysis of water and dissolved oxygen. Consequently, carboxylic acid groups can only be deprotonated in this system.

Literature reports of two pK_a values of carboxylate groups on GO of 4.4 and 6.6 [61], depending on the chemical/structural surrounding of the carboxylate group. It can be argued, that the acid groups with $\text{pK}_a = 6.6$ may be just partially dissociated, but FTIR spectra showed that at pH 5 and above no C=O vibration is visible at 1730 cm^{-1} , which is in accordance with our work.

6.5.4 Results from the Peak-fit Routine

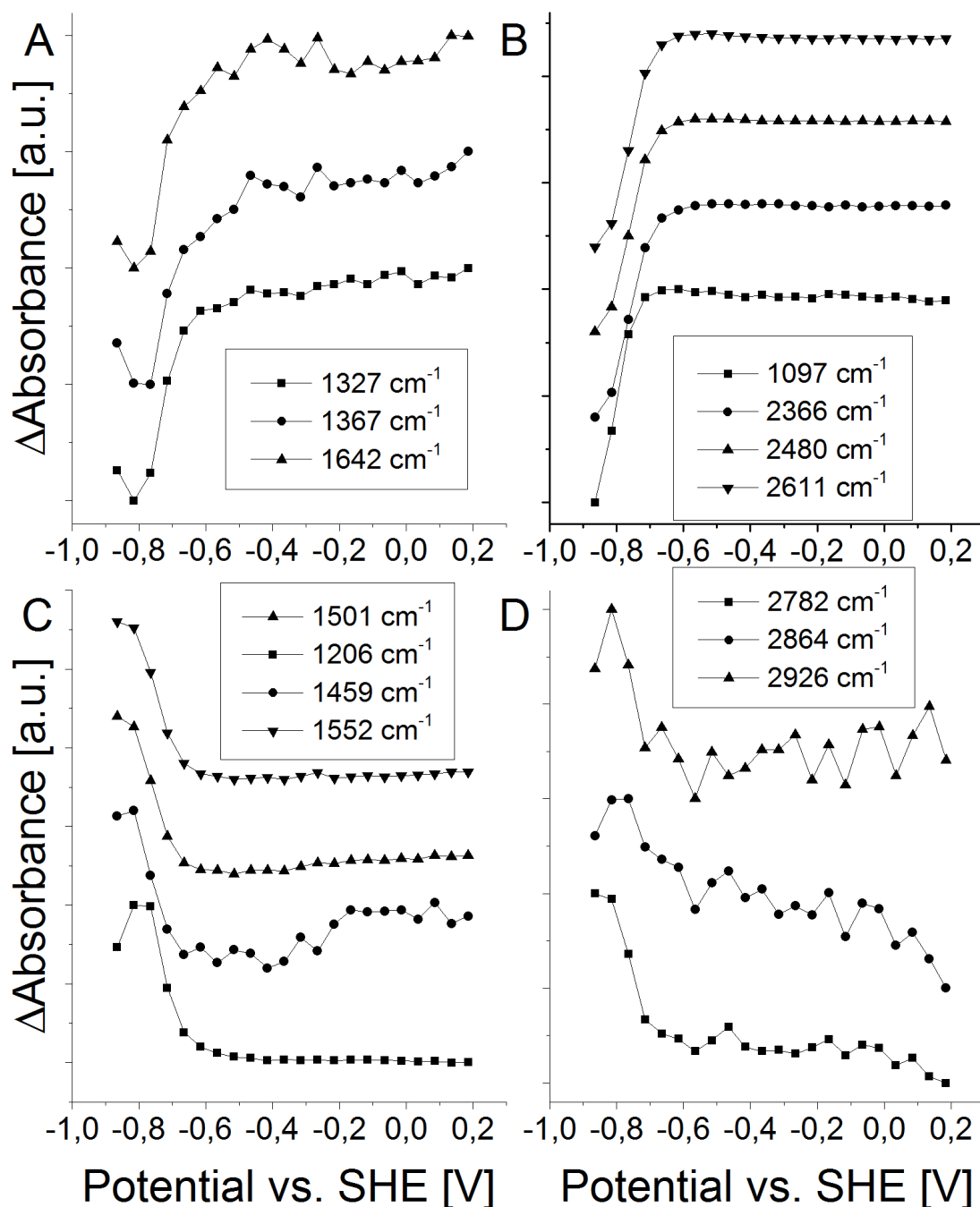


Figure 6.8: Peak fit results of the spectroelectrochemical data in D_2O . (A) Reduction of graphene oxide. (B) Reduction of α -reduced graphene oxide. (C) Formation of reduced graphene oxide. (D) Reduced graphene oxide shows the formation of aliphatic C-H bonds.

A classical peak fit routine was applied to the spectra of the measurements in D_2O . A closer look shows that the bands may be arranged into two clusters. One set shall be called α -rGO, which is synchronously reduced at -0.67 V (Fig. 6.8A). The other one we call β -rGO, which is reduced at a more cathodic potential of -0.70 V (Fig. 6.8B and 6.8C). A comparison of

Fig. 6.8 with the calculated clean spectra in Fig. 6.9B may be done for better understanding. Different oxygen containing groups with C–O bonds are constituted by the bands at 1327 cm^{-1} and 1367 cm^{-1} (Fig. 6.8A) and most probably can be assigned to the asymmetric stretching vibration of epoxides [1]. Their reduction takes place synchronously at slightly less overpotential than the bands of the second set (Fig. 6.8B).

The asymmetric COO^- stretch vibration is represented by the band at 1642 cm^{-1} in the first set, shown in Fig. 6.8A. This wavenumber may not be taken too quantitatively. A comparison with the spectra shows, that this band corresponds to the one at 1600 cm^{-1} . The shift in wavenumber is an artefact because of the insufficient peak separation of the used peak fit routine. MCR-ALS delivered clearer results, which is reported in section 6.5.5.

The bands at 2366 cm^{-1} , 2480 cm^{-1} , and 2611 cm^{-1} are the most intensive ones in Fig. 6.8B. They represent the O–D stretching vibrations of various oxygen containing functionalities in GO, like alcoholic groups. However, the solvent also absorbs strongly at these wavenumbers. A clear connection of these bands to the reduction of GO was shown by MCR-ALS in section 6.5.5. Comparable spectral features at higher wavenumbers were observed in the measurements in the non-deuterated electrolyte. The band at 1097 cm^{-1} is correlated to the second band set, which is the formation of β -rGO and the reduction of α -rGO. It represents the C–O vibration of alcoholic or epoxide groups. Both wavenumbers are in accordance with the respective literature [36, 43, 103].

The bands in Fig. 6.8C are increasing and correspond to the generation of rGO. A stepwise reduction can be surmised in Figs. 6.8A and 6.8B, which is not possible in Fig. 6.8C. Section 6.5.5 discusses MCR-ALS results, which take the synchronicity bands into account and confirm this interpretation. The cyclic voltammetry in section 6.5.1 shows a cathodic wave between -0.67 V and -0.8 V , which consists of several hardly resolvable reduction waves. Aromatic groups start generating at a potential negative of -0.70 V . This can be observed in the bands at 1552 cm^{-1} , 1501 cm^{-1} , and 1459 cm^{-1} . The skeletal vibrations of the conjugated lattice are represented at 1552 cm^{-1} , i.e. sp^2 -carbon bonding, resulting in an increase of conductivity [68, 114].

The bands at 1501 cm^{-1} and 1459 cm^{-1} were assigned to substituted aromatic regions. Nevertheless, the band at 1206 cm^{-1} increases earlier at a potential of -0.67 V . There the bands in Fig. 6.8B were reduced.

1206 cm^{-1} represent a C–O group generated due to the reduction of COO^- . A slight decrease of the absorption at the cathodic reverse potential affirms that. This COO^- group is most probably transformed into an alcoholic group. Consecutively, it is reduced at more

cathodic potentials. Section 6.5.5 supports this interpretation.

Another interesting observation, which is only possible in the deuterated electrolyte, is the behaviour of aliphatic regions, which are represented by the C–H stretching vibrations at 2782 cm^{-1} , 2864 cm^{-1} , and 2926 cm^{-1} (Fig. 6.8D) [91]. Aliphatic hydrogen is not exchanged by deuterium in D_2O , because it does not underlie a dissociation equilibrium. These bands are normally overlapped by the O–H stretching vibrations, which are now shifted to the O–D stretching vibrations at lower wavenumbers. The fact that aliphatic regions generated during the reduction of GO can be explained in that way that GO contains defects such as five- and seven-membered rings (from the synthesis procedure), which result in the formation of aliphatic regions, and thus C–H bonds.

6.5.5 Multivariate Curve Resolution

Based on a principle component analysis [52] and the above described peak-fit method it can be assumed that three species are involved in the electrochemical reduction of GO. Section 6.5.4 interpreted the reduction mechanism based on the behaviour of single bands. Nonetheless, it is actually not of importance how single bands behave, but the reactants, intermediates, and products, which are GO, α -rGO, and β -rGO.

Their concentration-potential dependence is displayed in Fig. 6.9A.

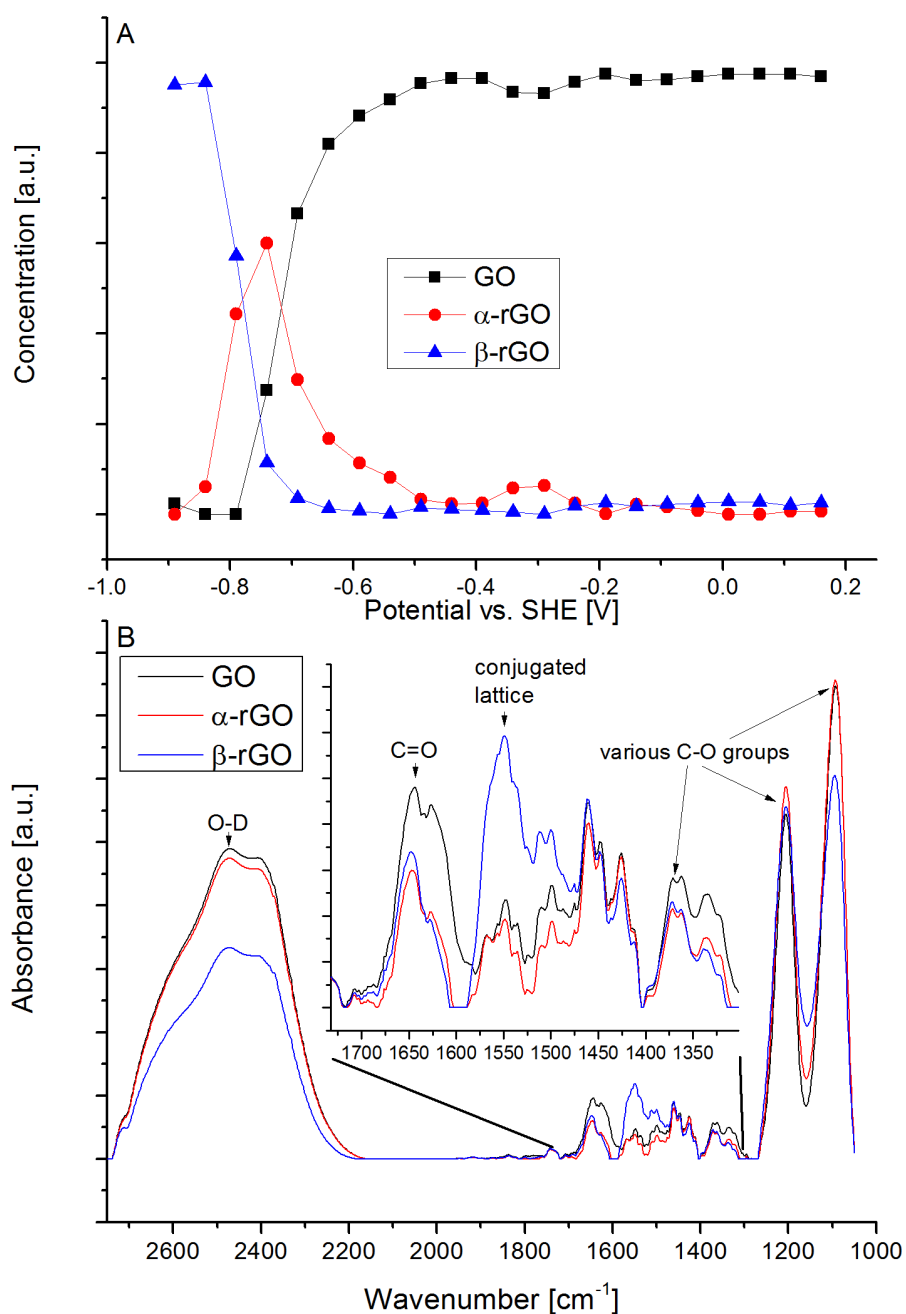


Figure 6.9: Results of the MCR-ALS evaluation of the spectroelectrochemical results. (A) Concentration profiles. (B) Clean spectra.

The cathodic reduction of GO occurs in two steps. Initially COO^- groups of GO (black curve) are reduced to α -rGO (red curve). Further, α -rGO is reduced to β -rGO (blue curve). The spectral changes take place in the same potential region as the reduction waves at -0.75 V to rGO above the ZnSe-surface of the ATR crystal (Fig. 6.4).

The peak fit routine, which is discussed in section 6.5.4, shows the trend of various bands. The MCR-ALS results do not just deliver the concentration profiles of the reactants, but also the clean IR-spectra of GO, α -rGO, and β -rGO (Fig. 6.9B).

The spectra correspond to the already discussed results and enable even more comprehension of the electrochemical reduction mechanism of GO. The initial step is defined by the decrement of carboxylate groups. This feature was observed between 1600 cm^{-1} and 1700 cm^{-1} . The peak shape and the position emphasise that carboxylate groups exist deprotonated.

Below 1400 cm^{-1} , several features can be assigned to different groups containing C–O bonds. The reduction of carboxylate groups in GO should result in the generation of C–O bonds in α -rGO. This may be assumed in a minor increase of the band at appr. 1200 cm^{-1} . Concurrently with the reduction of α -rGO to β -rGO it decreases again.

C–O bonds are present in various chemical groups, which behave electrochemically different. The Lerf-Klinowski model [65] states the presence of alcoholic groups, carboxylic acid groups, and epoxides. All of them contain C–O bonds. It is likely that the real structure of GO is even more complicated. Thus some C–O bonds are reduced in a first reduction step from GO to α -rGO between 1300 cm^{-1} and 1400 cm^{-1} and others are reduced in a second reduction step from α -rGO to β -rGO below 1300 cm^{-1} .

The second reduction step, which is from α -rGO to β -rGO, is defined by two features: the reduction of alcoholic groups and the formation of a π -conjugated lattice. The decrease of the O–D stretch vibration between 2200 cm^{-1} and 2700 cm^{-1} is associated to the reduction of the alcoholic groups. They decrease together with the C–O band at appr. 1100 cm^{-1} . Therefore, this band can be assigned to a C–OD vibration. The formation of the π -conjugated lattice is observed around 1550 cm^{-1} .

6.6 Conclusion

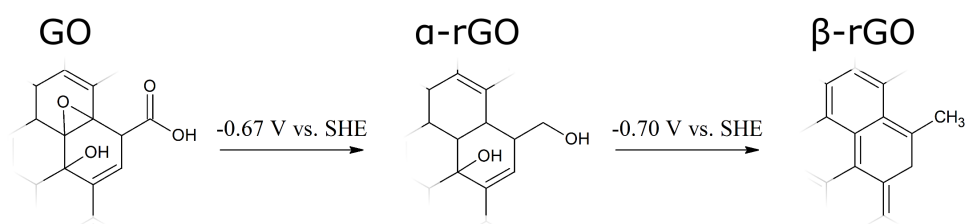


Figure 6.10: Mechanism of the electrochemical reduction of graphene oxide.

The cathodic reduction of GO in aqueous media was discussed. Cyclic voltammetry showed two reduction waves. One referred to the gold grid surface, another one to the regions directly on the ZnSe crystal surface between the grid fingers. This region directly on the ZnSe was monitored by *in-situ* FTIR spectroscopy. The spectroelectrochemical data was evaluated by a peak fit routine and Multivariate Curve Resolution-Alternating Least Squares. It was shown that the reduction takes place in a two step mechanism (Fig. 6.10). Initially, COO^- are reduced to C-O bonds. The resulting product, α -rGO, was reduced itself to β -rGO. In this second step C-O bonds and O-D bonds were reduced. They corresponded to alcoholic groups.

Chapter 7

Summary and Conclusion

Graphene Oxide is obtained by the oxidation and consequent delamination of graphite [15, 48]. It was known as graphitic acid since the mid of the 19th century and underwent a renaissance since the hype about graphene a few years ago [22].

Initially it was suggested as a precursor of graphene [30, 32]. Over time, people noticed its value as a nanomaterial itself [22]. In contrast to graphene it is an insulator, but can also be made conductive, when it is reduced [32]. Different defects are present in a high density and affect its electrochemistry. Also the manifold possibilities of chemical modification make it relevant for many branches in science and engineering.

However, the use of this material requires comprehensive knowledge and understanding of it. This work has made a contribution to the elucidation of the reduction mechanism of GO. The preparation of coatings as well as the reduction mechanism of various methods, and the characterization of the final products were discussed.

7.1 EQCM Study of the One-Step Approach

The generation of rGO coatings can be done via two routes: the one-step approach, where the coating and the reduction takes place in one step, and the two-step approach, where the coating and the reduction are two independent steps [98]. In the first part of this work, the one step approach was monitored with an EQCM.

The EQCM is an electrochemical *in-situ* device, which allows to monitor mass changes while running an electrochemical experiment [17]. In this study, the working electrode was Pt. GO was synthesized by a modified Hummers' method [108] and dispersed in phosphate buffer solution. The pH was adjusted between 6 and 9.

The working electrode was polarized anodically and cathodically. In both cases a mass deposition, which originated from GO, could be observed. It is intuitive that the mechanism of the GO deposition must follow different pathways. This was also indicated by the mass vs. potential curves.

Linear potential sweep and potential step experiments showed that in the anodic case GO was adsorbed on the electrode at appr. 1.5 V, which is at the beginning of the electrolyte decomposition (Fig. 7.1 anodic pathway). At higher overpotentials, the gas evolution repels the adsorbed layer. GO is a polyanion - especially at elevated pH - and its adsorption is of

mainly electrostatic nature and can only be sustained as long as the electrode is polarized. As soon as it is switched back to the open circuit potential, it is desorbed immediately.

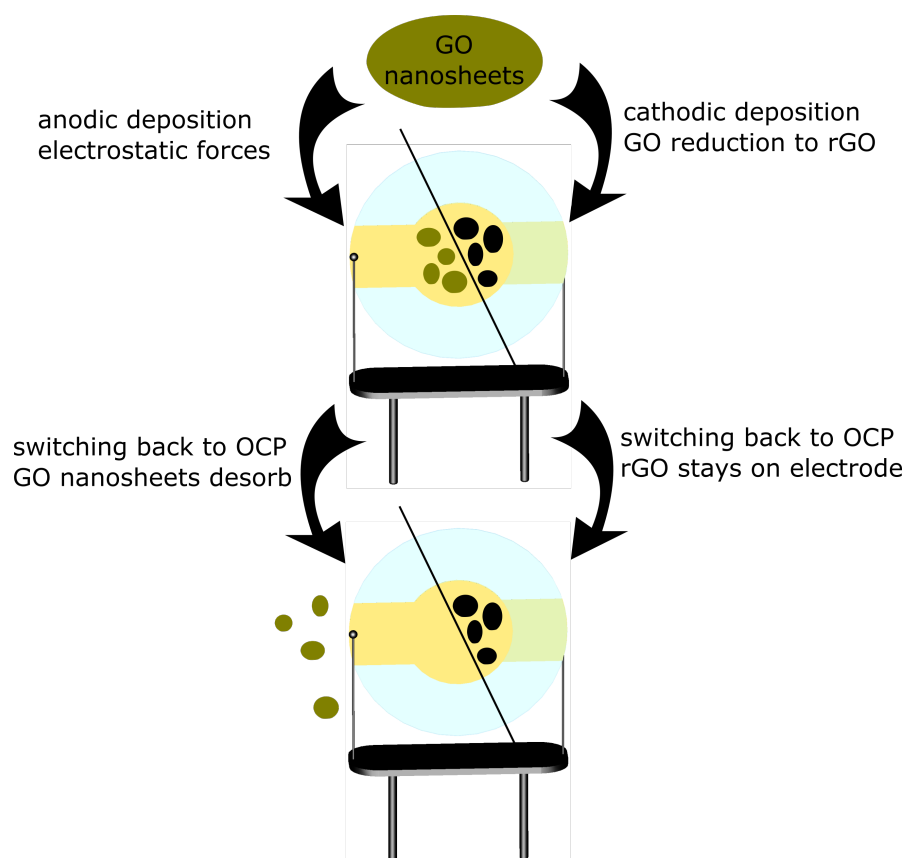


Figure 7.1: Mechanism of the anodic (left) and cathodic (right) deposition of graphene oxide.

The adsorption of GO on a cathodically polarized electrode behaves significantly different (Fig. 7.1 cathodic pathway). Negative of the point of zero charge, it cannot be of electrostatic nature because of the anionic nature of GO. At appr. -0.5 V, GO undergoes an electrochemical reduction. The product - rGO - is not dispersible in the buffer solution anymore and precipitates onto the Pt electrode. Consequently it adheres also on the electrode, when the potential is switched back to the open circuit potential. If the overpotentials are too high, the GO reduction and adsorption is inhibited, but GO is not repelled anymore.

Both - the anodic and the cathodic GO adsorption - occur in the same potential region as the respective reduction or oxidation of phosphate, which is present in the electrolyte and functions as buffer. Spectroelectrochemical FTIR measurements showed that this is a coincidence. Phosphate is neither involved in the cathodic nor in the anodic adsorption of GO.

7.2 Preparation of Graphene Oxide Coatings

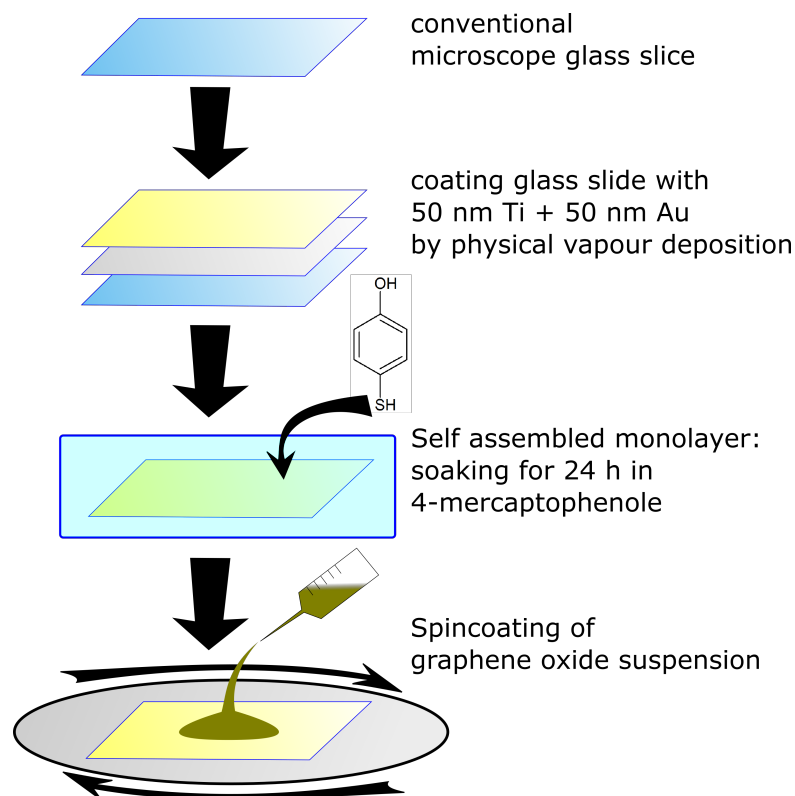


Figure 7.2: Schematic sketch of the coating routing of a glass slide with graphene oxide.

The preparation of homogeneous, reproducible GO coatings is a crucial task. The easiest way is just to dry a droplet of GO suspension on a substrate [14, 70, 105, 106]. This method is easy to perform and does not need any expensive equipment. Thus, it is frequently performed. However, the homogeneity and reproducibility of these coatings is poor.

In this work, the method of choice for preparing GO coatings is spincoating. The combination of this technique with 3D-printing made it possible to coat almost any flat sample geometry. The choice of the right parameters made it possible to control the thickness of smooth coatings.

Glass and ZnSe substrates could be coated directly, because aqueous GO suspensions wetted the surface. With gold substrates - due to their hydrophobicity - this was not directly possible. To overcome this problem a self assembled monolayer was prepared on the gold surface before spin coating. This led to complete wetting of the GO suspensions on the substrate and made spincoating possible. A sketch of the whole synthesis procedure can be seen in Fig 7.2.

A further essential task was the evaluation of the final thicknesses of the coatings. The

challenge is that conventional methods, like the preparation of a cross section, are not applicable. The thickness of the coatings is a few nanometres and therefore hardly resolvable for most electron microscopes. Additionally GO coatings can be easily harmed by an electron beam. Further, the mechanical stability of the coating is not sufficient for preparing a cross section

Here, a groove was cut into the coating with a femtosecond laser. The energy of the laser was adjusted in such a way, that the GO coating was ablated, but the underlying gold reflected the laser beam and stayed intact (perfect etch stop). These samples were investigated with an atomic force microscope to determine the depth of the groove and thus the thickness of the coating.

One spincoating step produced a GO coating of 3 nm, which corresponds to three monolayers of GO. The repetitive applications of spincoating steps made it possible to produce thicker coatings, e.g. three steps resulted in a final thickness of appr. 10 nm.

7.3 Reduction of Graphene Oxide with the Femtosecond Laser

GO coatings were prepared via spincoating on glass and gold substrates. These coatings were reduced with a fs-laser at different fluences. The material modification could be directly observed under an optical microscope. Depending on the substrate and whether GO was reduced or ablated, the reflectivity of the material changed. By evaluating the brightness of the irradiated spots ablation thresholds could be determined for glass $F_{th,a} = 0.04 \text{ J/cm}^2$ and for Au $F_{th,a} = 0.08 \text{ J/cm}^2$.

The ablation of GO on glass substrates was observed at lower laser fluences than that on Au. Assuming a photothermal mechanism [113] it is reasonable, that the Au substrate can dissipate accumulated heat in contrast to glass. Thus, more energy, i.e. fluence, is required for the ablation of the GO coating. A similar mechanism may be assumed for the reduction of GO, although the reduction thresholds were below the lowest measured laser fluence and could therefore not be quantified.

The GO reduction was verified by an SECM. For this measurement it was mandatory that the substrate was an electrical conductor. Therefore it was only performed on the Au substrate. Also the areas, which were irradiated with the lowest fluences and showed neither modification under the optical microscope nor via Raman spectroscopy, showed significant electrochemical activity in comparison to the untreated GO areas. At appr. 0.08 J/cm^2 , i.e.

in the same region as the changes of the Raman spectra occurred, an increasing electrochemical activity could be observed. The highest activity was measured at 0.101 J/cm^2 . At this point the reduction was maximum and the ablation did not expose significant Au areas. At higher fluences more Au was exposed, which showed a lower electrochemical activity than rGO. Thus the overall measured activity decreased as well.

Raman spectroscopy showed that between the reduction and ablation, the defect density is increased significantly. These three processes overlap with each other. On gold a wider window for the laser fluence for the reduction of GO was found. The generation of more defects was on glass more significant than on Au. On gold these effects were negligible small. The heat dissipation on gold seems to have a positive effect for the final structure of the product.

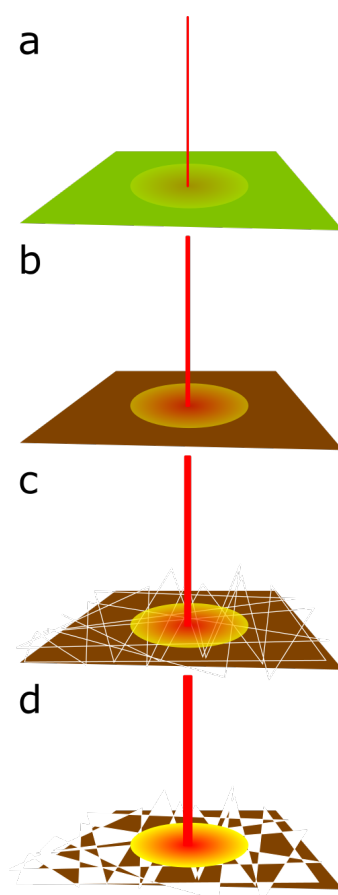


Figure 7.3: Modification of graphene oxide coating by fs-laser irradiation at increasing fluence. (a) No modification. (b) Reduction of graphene oxide. (c) Introduction of defects. (d) starting ablation

Conclusively the fs-laser modification of GO can be summarized in four steps, which were sketched in Fig. 7.3. At first GO is irradiated and nothing happens (Fig. 7.3a). At higher

fluences GO is reduced to rGO (Fig. 7.3b), this was confirmed by an SECM. This process is overlapping with the generation of defects (Fig. 7.3c), which is a continuous process, followed by ablation (Fig. 7.3d). The ablation thresholds were determined for glass $F_{th,a} = 0.04 \text{ J/cm}^2$ and for Au $F_{th,a} = 0.08 \text{ J/cm}^2$.

7.4 Reduction of Graphene Oxide with the Scanning Electrochemical Microscope

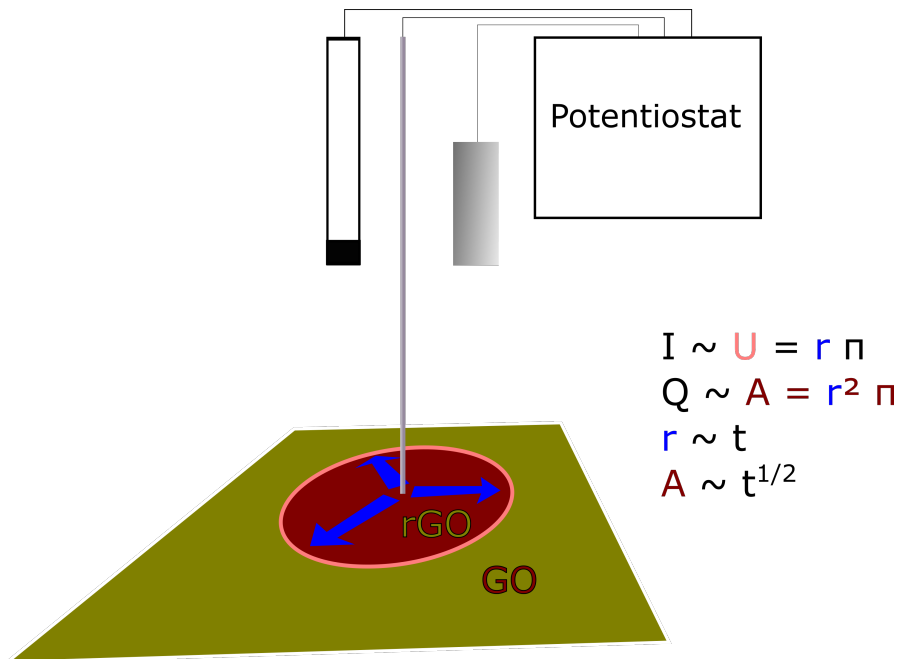


Figure 7.4: Mechanism of the local reduction of graphene oxide with a scanning electrochemical microscope.

For the local reduction of GO coatings on glass, a cathodically polarized microelectrode of an SECM was approached precisely onto the GO surface. Initially, the microelectrode reduces directly the GO coating, which is in contact with it. Further, this just reduced GO acts itself as an electrode and reduces the surrounding GO. This process proceeds, such that an rGO spot starts growing in the GO coating (Fig. 7.4).

It was tried to control the diameter of the spot. A straight forward approach would be to adjust the reduction time. This did not work, because the mechanical contact to the sample is not exactly reproducible and affects the growing speed of the spot significantly.

The next approach was to adjust the spot diameter by controlling the consumed charge Q . The amount of species is constant over one unit area as long as the thickness of the sample

does not change, like it was the case in this study. Therefore, the charge is proportional to the area A of the rGO spot and is suitable for controlling the diameter of the rGO spot. Further considerations showed that the area is proportional to the square of the radius r^2 . The current is proportional to the circumference and thus the radius $I \propto U \propto r$. The radius of the spot grows with constant speed and is thus proportional to the elapsed reduction time. The rGO spots were characterized via Raman spectroscopy. A peak fit analysis and a true components analysis showed that the positions and the intensity ratio of the D and G bands change during the reduction process. The amount of disorder in the structure increases during the reduction process.

7.5 The Mechanism of the Electrochemical Reduction of Graphene Oxide

The electrochemical reduction of GO is a green and easy to perform alternative to other reduction methods [43]. Thus, it is frequently used to produce rGO coatings with specified properties [22]. To control the properties of the final product it is necessary to gain understanding of the underlying mechanism.

To investigate this mechanism a spectroelectrochemical technique was chosen. A thin gold grid was evaporated onto an ATR prism and served as working electrode. While running an electrochemical experiment, it was possible to gather IR spectra of the GO coating.

MCR-ALS [29, 52, 53] was used to evaluate the data. This technique, together with the use of a deuterated electrolyte, enabled to observe a two-step mechanism of the GO reduction (Fig. 7.5). These two steps were in such a narrow potential range of appr. 50 mV that it was not possible to make the same conclusion by a conventional peak fit routine in non-deuterated water.

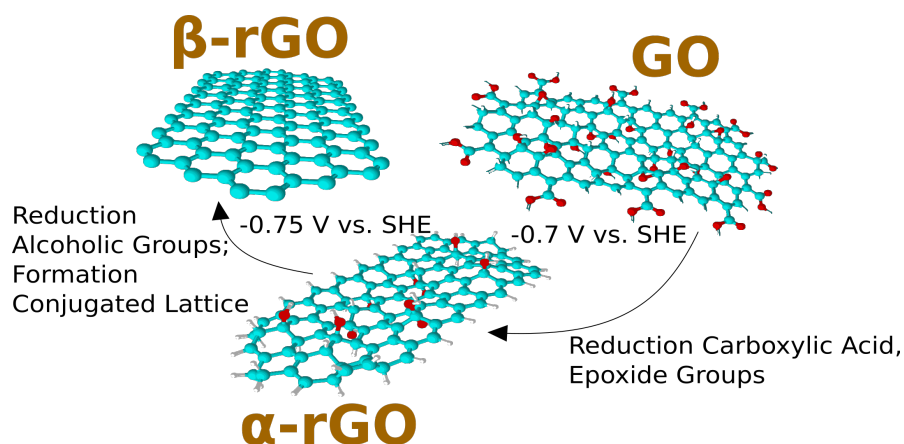


Figure 7.5: Mechanism of the electrochemical reduction of graphene oxide.

In a first step at -0.7 V GO is reduced to so-called α -rGO. Carboxylate functionalities and C–O bonds in epoxides are reduced. α -rGO is not responsible for the conductivity of rGO. Negative of -0.7 V , α -rGO is reduced to β -rGO. Here, mainly alcoholic groups are reduced and a π -conjugated lattice is partially restored. But also aliphatic regions could be detected. They are originating from defects in GO, like f.i. five- or seven-membered rings, which prevent the formation of an aromatic structure.

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Appendix A

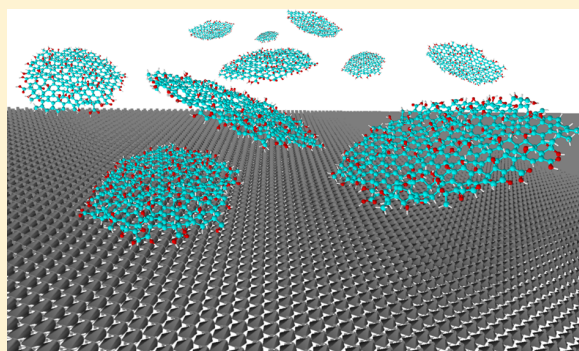
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QMB Study of the Electrochemistry
of Graphene Oxide on Platinum***

In Situ FTIR and in Situ QMB Study of the Electrochemistry of Graphene Oxide on Platinum

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ABSTRACT: The cathodic and anodic behavior of graphene oxide was investigated in aqueous suspensions on platinum. The anodic deposition relied on the polyanionic character of graphene oxide with increasing pH. It took place simultaneously with the oxidation of phosphate to peroxodiphosphate and the oxygen evolution. Scanning electrochemical microscopy showed an inhomogeneous anodic adsorption. The cathodic deposition is based on the reduction of graphene oxide to reduced graphene oxide, which showed reduced solubility. Anodic oxygen evolution led to the desorption of graphene oxide anions, whereas hydrogen evolution blocked further adsorption of reduced graphene oxide but caused no desorption.



INTRODUCTION

Since the first report of the preparation of graphene by mechanical exfoliation¹ many applications of this very versatile material have been proposed, for example, for sensor materials,² electronic applications,³ or corrosion protection.⁴ Graphene exhibits unique properties such as a zero band gap, impermeability to gases, even He and H₂, and the highest mechanical strength ever observed.^{5,6} Chemical vapor deposition (CVD)⁷ and mechanical exfoliation¹ are able to produce high-quality graphene. CVD is even able to produce graphene of almost any size; however, these methods are expensive or not scalable for mass production.

The reduction of graphene oxide (GO) is another possibility to obtain graphene on an industrial scale. The product is of poorer quality than pristine graphene according to the present state of the art due to defects introduced by the preparation procedures.^{8–10} Therefore, the technical term “reduced graphene oxide” (rGO) has been established. Several electrochemical methods have been developed for coating substrates with graphene-related materials¹¹ and the reduction of GO.¹² The coating of metal substrates can be performed by so-called “electrophoretic” deposition, either with a polymer as supporting agent^{4,13} or with a pure GO dispersion.⁸ Approaches to reduce GO electrochemically in aqueous or organic solutions have been described as well.^{9,10}

The electrochemical reduction of GO can be roughly divided into two strategies: In the two-step approach, the electrode is initially coated with GO (by drop casting, spin coating, etc.), and afterward this coating is reduced electrochemically.¹² In the one-step approach, GO is deposited and reduced directly from a suspension.¹² The electrochemical in situ investigation concentrated on the evaluation of the chemical function of GO/rGO.¹⁰

This study is concerned with the fundamentals of the electrochemical GO adsorption and reduction on platinum. Kinetic in situ data such as film growth in correlation to current density, together with homogeneity and conductivity information, is required to elucidate the electrochemical mechanism of these processes. This has not been realized systematically so far. In this study, therefore, a first in situ electrochemical investigation of the deposition of GO on platinum has been undertaken with an in situ electrochemical quartz microbalance (EQMB). In situ FTIR spectroscopy served to investigate the role of the electrolyte in the reduction mechanism of GO.

Mechanistic insights into the electrochemical adsorption and reduction mechanisms of GO could be attained with in situ investigations for the first time. For example, they showed that the reductive deposition of rGO takes place in parallel with the phosphate reduction and the hydrogen evolution in dependence of pH. The GO reduction stops once a particular rGO film thickness has been reached. The hydrogen evolution persists in the interstices of inhomogeneous rGO sheets.

EXPERIMENTAL SECTION

GO was prepared by a modified Hummer's method¹⁴ starting with natural graphite (325 mesh, Alfa Aesar). The as-prepared GO was cleaned by ultracentrifugation at 12 000 rpm corresponding to 21 000g, and washing with 1 M HCl and finally with deionized water. FTIR spectra of GO and natural graphite were recorded with a FTIR spectrometer (Bruker Vertex 70) equipped with a rock-solid interferometer and a

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DTGS detector. GO and natural graphite were dispersed in water and dried on a 2 mm thick ZnSe window. The IR spectra were recorded in transmission geometry with 2 cm^{-1} resolution.

A 66.7 mM Na-phosphate-buffered solution (PBS) was prepared to vary the pH between 6.2 and 8.2. One mg/mL GO was dispersed in PBS by ultrasonication for 30 min (Bandelin RK 510H). The final pH was checked with a pH/Ion meter (Metrohm 781). This solution was used for EQMB measurements (CH-Instruments 440A). Pt-coated 8 MHz AT-cut quartz wafers were employed (CH Instruments). An Ag/AgCl reference electrode and a Pt counter electrode were used. The Pt surface was cleaned by cycling in 0.1 M H_2SO_4 solution. All potentials are presented versus the standard hydrogen electrode (SHE) as U_{SHE} .

For in situ FTIR spectrometry, an external liquid-nitrogen-cooled LN-MCT detector was employed.¹⁵ The beam delivery optics were positioned on an aluminum breadboard in a CO_2 - and water-free air-flushed compartment. The in situ electrochemical cell was manufactured from Teflon. A conventional potentiostated three-electrode setup (potentiostat: Electrochemical Workstation, CH-Instruments 760C) with a platinum wire as counter electrode and an Ag/AgCl/3 M KCl electrode as reference electrode (+ 0.21 V vs SHE)¹⁶ were used. The working electrode was mounted on a glass tube precisely positioned relative to the ZnSe window by a digimatic micrometer head (Mitutoyo, no. 164-163) with a resolution of $1\text{ }\mu\text{m}$. The spectra were measured under p-polarization. The sampling time for each spectrum was 25 s.

In the scanning electrochemical microscopy (SECM) investigations, a microelectrode with $10\text{ }\mu\text{m}$ diagonal, a Ag/AgCl reference electrode, and a Pt counter electrode were employed (scanning electrochemical microscope CH-Instruments 920D). GO was dispersed in a 20 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution in 66.7 mM PBS by ultrasonication, as previously described.

RESULTS AND DISCUSSION

It was necessary to monitor the synthesis of GO according to the modified Hummer's method¹⁴ starting with natural graphite by FTIR spectroscopy (Figure 1). The obtained GO was characterized by identifying its absorption bands: O–H

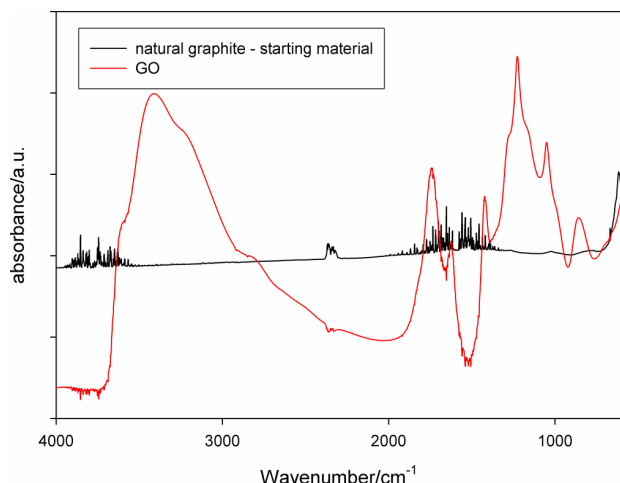


Figure 1. FTIR spectra of GO (red) and natural graphite (black).

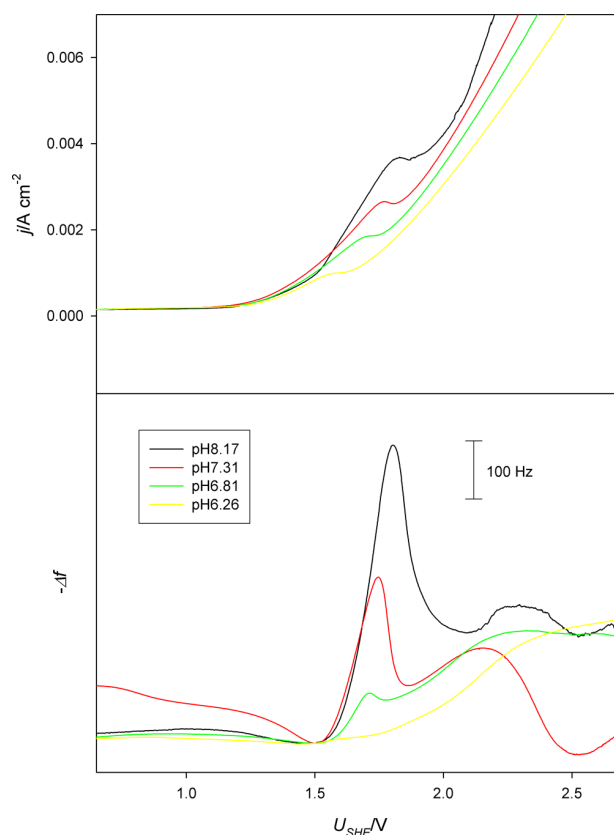
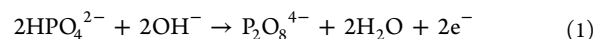


Figure 2. Linear anodic potential sweeps of GO dispersions. 66.7 mM Na-PBS, 1 mg/mL GO. Initial potential: individually measured OCP. Final potential: -2.79 V . Scan rate: 5 mV/s . Ag/AgCl reference electrode.

stretching at 3400 cm^{-1} , C=O stretching at 1740 cm^{-1} , skeletal vibrations due to adsorbed water at 1620 cm^{-1} , O–H deformation at 1420 cm^{-1} , C–OH stretching at 1220 cm^{-1} , and C–O stretching at 1050 cm^{-1} .¹⁷

Figures 2 and 3 show the EQMB results of linear potential sweeps in anodic direction. The current shoulder above 1.2 V with and without GO indicates the oxidation of phosphate to peroxodiphosphate¹⁸



This reaction occurs concurrently with the oxidation of water to oxygen on oxidized platinum (PtO_2)¹⁹ represented by the general anodic current rise. This current increases with pH due to the rising concentration of the reaction partner OH^- .

GO exhibits functional oxygen groups such as carboxyl groups, especially at the sheet edges.²⁰ These groups can be deprotonated at high pH to produce a polyanion. Because of its negative charge in alkaline environment, GO can be adsorbed anodically on the electrode.

The mass increase (frequency reduction) around 1.7 V is solely due to the adsorption of these partially deprotonated GO anions (Figure 2). In the absence of GO, no frequency change was observed (Figure 3). The extent of the GO adsorption increases with pH (Figure 2) because of the rising amount of negative charges on the GO anion sheets. This GO anion adsorption takes place concurrently with the phosphate oxidation (eq 1) and the oxygen evolution. The EQMB frequency data are interpreted qualitatively. They cannot be

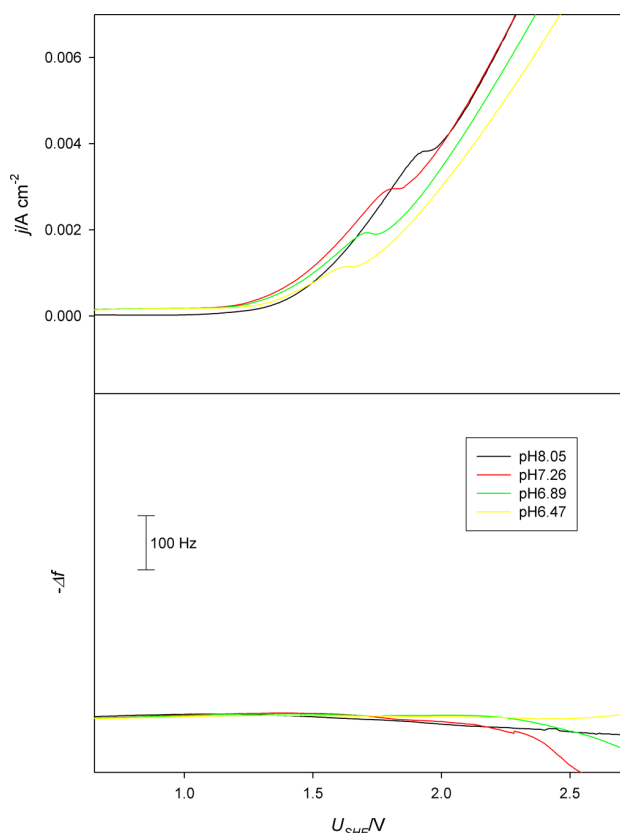


Figure 3. Linear anodic potential sweeps of blind samples. 66.7 mM Na-PBS, 0 mg/mL GO. Initial potential: individually measured OCP. Final potential: 3.21 V. Scan rate: 5 mV/s. Ag/AgCl reference electrode.

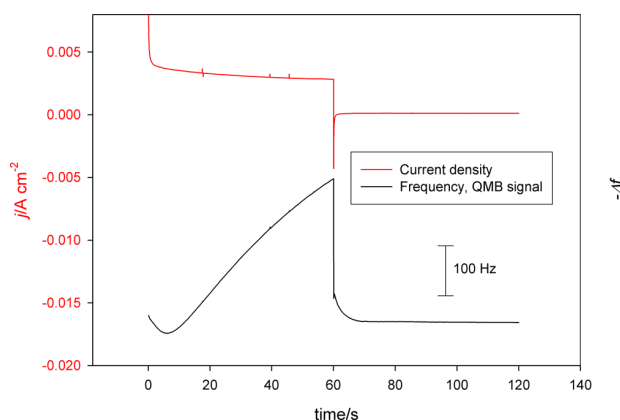


Figure 4. Chronoamperometry measurement of GO dispersion; anodic. 66.7 mM Na-PBS, pH 8.2, 1 mg/mL GO. Potential: 1.71 V for 60 s, then back to previously measured OCP for 60 s. Ag/AgCl reference electrode.

converted into mass quantitatively because GO anions are highly hygroscopic and strongly solvated at the anionic functions. Assuming rigid unsolvated pristine graphene with a 2D density of $6.87 \times 10^{-4} \text{ g/m}^2$ (according to a bond length of 0.142 nm),²¹ a perfect monolayer would result in -99 Hz according to the Sauerbrey equation²² in the present setup. According to this, the anodic and cathodic film growth is on the order of a few monolayers. Actually, the GO anionic sheets may

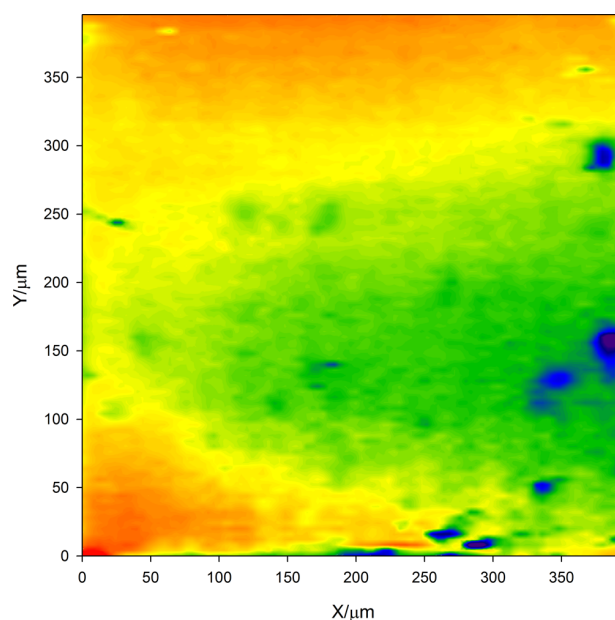


Figure 5. Scanning electrochemical microscopy (SECM) measurement of a GO dispersion; anodic. 66.7 mM Na-PBS, 1 mg/mL GO, 20 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$. 1.71 V substrate potential, -0.09 V probe potential. Scan rate: $40 \mu\text{m/s}$. Pt microelectrode: $10 \mu\text{m}$ diameter. Pt substrate electrode, Ag/AgCl reference electrode.

not be positioned flat on the substrate but may extend into the electrolyte. Thus, they may either not couple rigidly to the electrode surface, resulting in smaller frequency changes, or may carry additional solvation molecules of unknown quantity, leading to an increased frequency signal.

Above 1.8 V, the mass decreases again, indicating the desorption of GO from the PtO_2 -covered electrode because of the oxygen evolution. Chronoamperometry measurements were performed at the potential of 1.71 V and pH 8.2, where GO anion adsorption took place together with the phosphate oxidation (eq 1) and the oxygen evolution (Figure 4).

After the potential step from the open-circuit potential (OCP) to 1.7 V, a continuous increase in the mass due to GO anion adsorption was observed. Upon the return to the original potential, a practically complete desorption of GO anions occurred.

SECM at a substrate potential of 1.71 V was undertaken to investigate the homogeneity of the GO films. After 60 s of adsorbing GO, the SECM scan was performed. It can be seen that the GO adsorption and the surface conductivity were inhomogeneous (Figure 5). Because GO is an insulator, the feedback should be negative if the sample was completely covered with GO; however, probe approach curves showed a positive feedback. That is, the adsorbed GO film was porous so that diffusion of the redox-active species $[\text{Fe}(\text{CN})_6]^{3-}$ could take place. Because of this, the GO film could not passivate the electrode surface. Water could still be oxidized and O_2 bubbles were generated, which removed the GO layer mechanically at higher potentials.

A current shoulder on the hydrogen evolution currents in linear cathodic sweeps was observed with and without GO negative of -0.4 V (Figures 6 and 7). This can be correlated with the reduction of phosphate to phosphite around a pH-dependent potential of $U_{\text{SHE}} \approx 0.48 \text{ V}$ (pH 8)²³

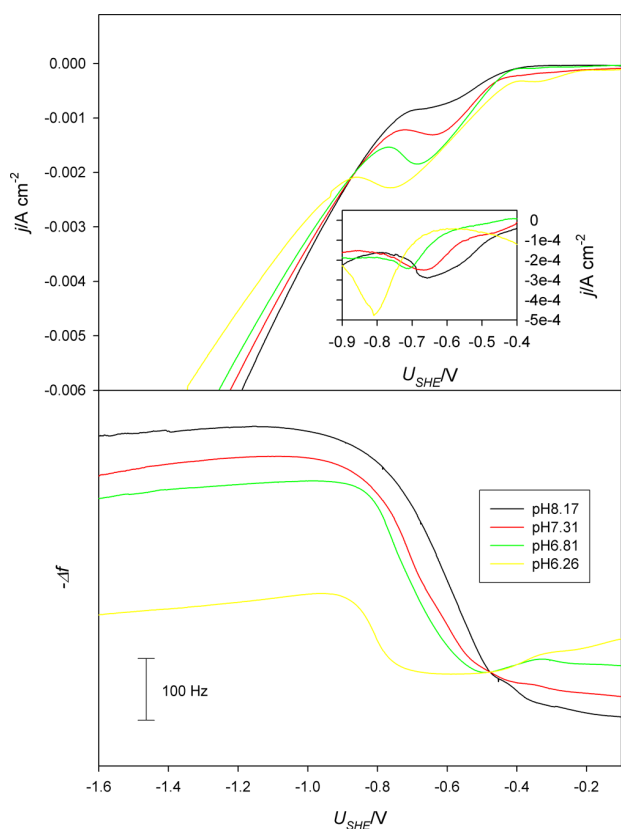


Figure 6. Linear cathodic potential sweeps of GO dispersions. 66.7 mM Na-PBS, 1 mg/mL GO. Initial potential: individually measured OCP. Final potential: -2.79 V. Scan rate: 5 mV/s. Ag/AgCl reference electrode. Inset in upper graph: net current density of GO reduction: difference of current densities with and without GO (Figure 7).



The phosphate reduction current is reduced by increasing pH (Figures 6 and 7).

The current of the measurement without GO can be subtracted of the current of the measurement with GO. The results of this procedure are shown in the inset of Figure 6. The reduction current densities of GO are an order of magnitude less than the phosphate reduction current densities. The GO reduction current waves correlate perfectly with the mass increase steps.

Both the GO and the phosphate reduction take place concurrently with the proton reduction (Figures 6 and 7). Remarkably, the proton reduction reaction still increases with negative potential, even though the rGO film formation stopped. rGO films seem to be a poor catalyst for the hydrogen evolution by analogy to graphite in contrast with Pt still accessible to the electrolyte in the interstices of the adsorbed rGO sheets.

The EQMB results show that between -0.3 (pH 8.17) and 0.7 V (pH 6.26) the mass increased only in the presence of GO anions (Figures 6 and 7). Therefore, this mass gain can be correlated with the adsorption of rGO. The mass starts leveling off between ca. -0.9 (pH 6.26) and -1.0 V (pH 8.17), suggesting that the reduction of GO and the adsorption of the product rGO stopped. The observed hydrogen evolution is expected to take place on the remnant defects of the rGO layer

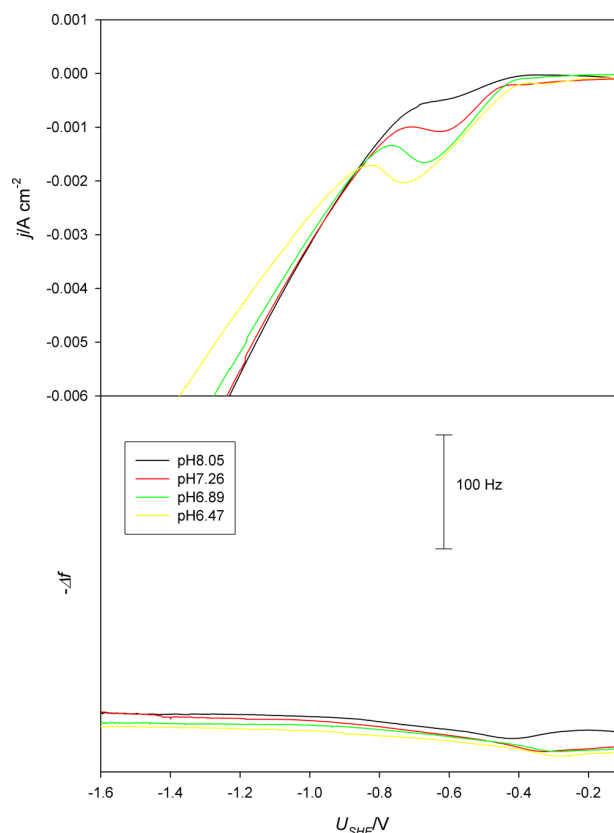


Figure 7. Linear cathodic potential sweeps of blind samples. 66.7 mM Na-PBS, 0 mg/mL GO. Initial potential: individually measured OCP. Final potential: -2.79 V. Scan rate: 5 mV/s. Ag/AgCl reference electrode.

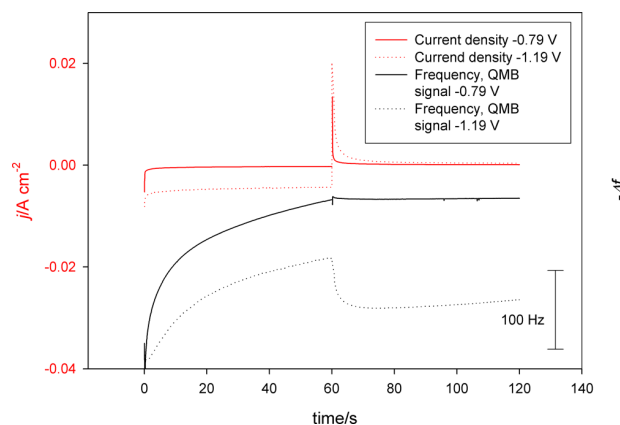


Figure 8. Chronoamperometry measurement of a GO dispersion, cathodic. 66.7 mM Na-PBS, pH8; 1 mg/mL GO. Potentials: -1.19 and -0.79 V for 60 s, then back to previously measured OCP for 60 s. Ag/AgCl reference electrode.

exposing catalytically active Pt areas. The catalytic influence on the GO reduction kinetics on either bare Pt or deposited rGO is going to be investigated. There are also reports that the hydrogen evolution may interfere with the adsorption status of rGO.^{17,24,25}

Because GO is a polyanion at elevated pH, the cathodic deposition has to follow a different mechanism than in the anodic potential region. Around -0.8 V, GO was reduced to

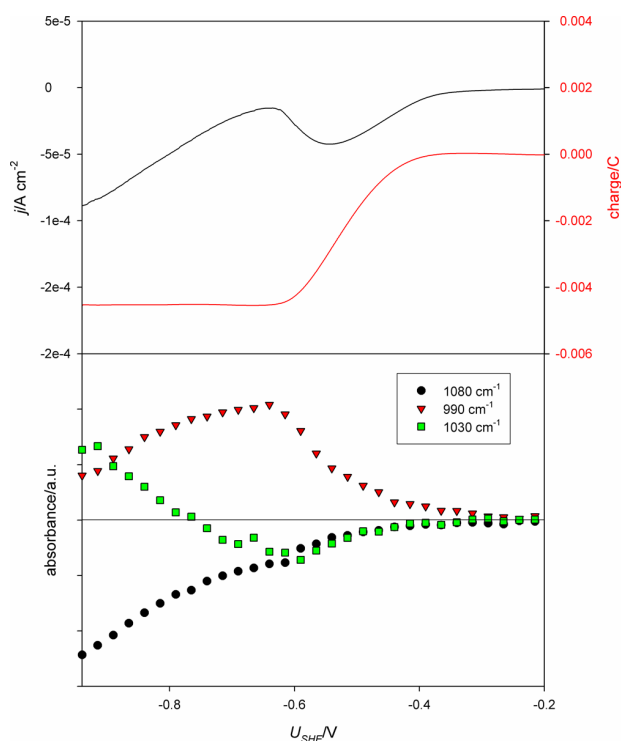


Figure 9. FTIR spectra: in situ linear cathodic potential sweep. 66.7 mM PBS; 0 mg/mL GO. Initial potential: individually measured OCP. Final potential: -0.94 V. Scan rate: 1 mV/s. Pt working electrode, Ag/AgCl reference electrode, Pt counter electrode. Upper graph: current density (black); charge calculated by baseline fitting (subtraction of H_2 evolution) and peak integration.

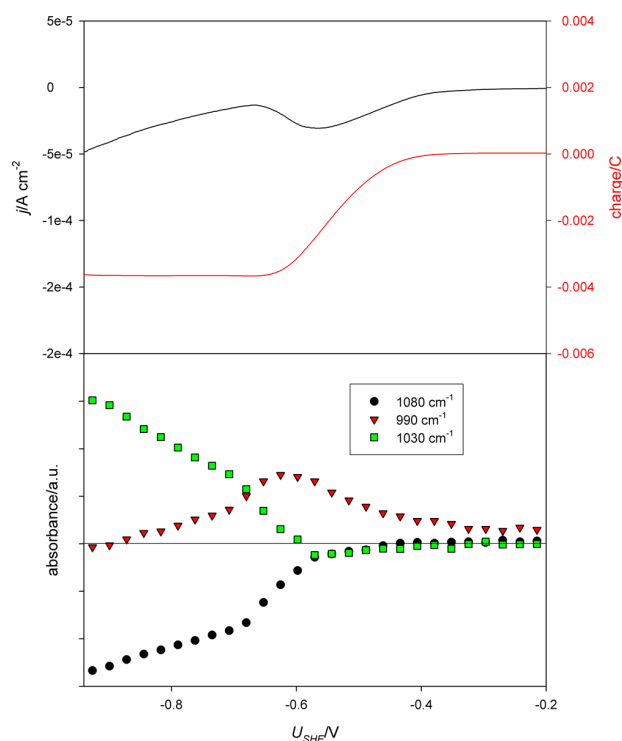


Figure 10. FTIR spectra: in situ linear cathodic potential sweep. 66.7 mM PBS; 0.1 mg/mL GO. Initial potential: individually measured OCP. Final potential: -0.94 V. Scan rate: 1 mV/s. Pt working electrode, Ag/AgCl reference electrode, Pt counter electrode. Upper graph: current density (black); charge calculated by baseline fitting (subtraction of H_2 evolution) and peak integration.

rGO.²⁴ The mass of adsorbed GO increased with pH. This can be correlated with the solubility of GO. At lower pH values, GO tends to precipitate.²⁶ Even if GO can be hardly separated from the solution by usual centrifugation, it can form coagulations. Therefore, the concentration of solvated GO anions occurring as single sheets increased at higher pH, and the electrochemical reduction rate (current density) of GO to rGO rose. rGO is less soluble than GO and therefore adheres to the electrode.

This was confirmed by another chronoamperometric measurement at pH 8.2 (Figure 8, solid lines): at -0.8 V, the mass increased slowly up to a saturation level, which is on the order of an rGO monolayer including some solvation water. This suggests that the diffusion retards the GO reduction rather than the electron transfer to the oxygen containing groups up to about a monolayer. The potential step back to the OCP does not change the adsorption status of rGO. This, however, is accompanied by a fast exchange of solvated Na^+ cations by solvated phosphate ions obviously not hindered by the presence of the rGO sheets.

At an even higher overpotential, at -1.2 V, GO was reduced to rGO to a lesser extent, suggesting mechanical interference of the synchronic hydrogen evolution process. Also, the return to the OCP led to a contrasting behavior, the reduction of mass. That suggests that the mass increase at -1.2 V was composed of both rGO and adhering gaseous hydrogen, which disappears at the OCP, causing the observed mass decrease.

In situ FTIR spectroscopy was employed to answer the question of whether the reduction of GO was influenced by the

concurrent phosphate reduction. The IR signal of phosphate (1080 cm^{-1})²⁷ was reduced in the presence of a pure PBS solution (Figure 9). This band can be assigned to the symmetric P–O stretch vibration.²⁸ The signal of $\text{H}_2\text{PO}_3^{3-}$ (990 cm^{-1}) increased in accordance with the respective redox reaction. Shifting the potential negatively increased the signal of HPO_3^{2-} (1030 cm^{-1}) and decreased that of $\text{H}_2\text{PO}_3^{3-}$. The broad band at 1030 cm^{-1} is correlated with the asymmetric P–O stretch vibration.²⁹ Negative of -0.8 V, the pH increased above the pK_a of the couple $\text{H}_2\text{PO}_3^{3-}/\text{HPO}_3^{2-}$ at 6.59.³⁰ When GO was present (Figure 10), the same phenomenon could be observed. The IR data show that the pH is less stable.

CONCLUSIONS

Mechanistic insights into the electrochemical adsorption and reduction mechanisms of GO could be attained. A phosphate pH buffer served as electrolyte.

The electrochemical deposition of GO can be performed anodically in the range of $+1.5$ and $+1.8$ V. The anodic adsorption of the GO polyanion occurs simultaneously with the phosphate oxidation. The GO adsorption is accelerated with increasing pH possibly due to a better solubility of the anion sheets. Above 1.8 V, a GO mass decrease indicated the displacement of GO by the oxygen gas formation. Even though GO should passivate the electrode, SECM results demonstrated that the films are inhomogeneous, thus allowing oxygen evolution at Pt.

The reduction in rGO and its deposition can be performed cathodically negative of -0.5 V at platinum. In situ

investigations showed that the reductive deposition of rGO takes place in parallel with the phosphate reduction and the hydrogen evolution at moderate overpotentials. Increasing the pH accelerates the adsorption of GO. The GO reduction is inhibited once a particular rGO film thickness has been reached. The hydrogen evolution persists in the interstices of these rGO sheets.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS

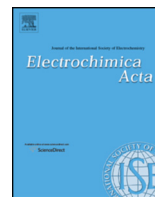
CVD, chemical vapor deposition; EQMB, electrochemical microbalance; FTIR, Fourier transform infrared; GO, graphene oxide; rGO, reduced graphene oxide; SECM, scanning electrochemical microscopy; SHE, standard hydrogen electrode

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Appendix B

Publication Electrochimica Acta: A
Multivariate Curve Resolution
evaluation of an in-situ ATR-FTIR
spectroscopy investigation of the
electrochemical reduction of
graphene oxide



A Multivariate Curve Resolution evaluation of an *in-situ* ATR-FTIR spectroscopy investigation of the electrochemical reduction of graphene oxide



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ABSTRACT

Graphene oxide (GO) is a potential precursor for graphene. The electrochemical reduction of graphene oxide on electrode interfaces is a low-cost and green approach. The mechanism of the reduction, as well as the final structure of the reduced form have been the focus of the present study. In this work, the reduction of graphene oxide was investigated by *in-situ* spectroelectrochemistry. FTIR spectroscopy showed the generation and degeneration of oxygen containing functional groups and C=C bonds. The evaluation of these results was done via Multivariate Curve Resolution - Alternating Least Squares (MCR-ALS) to assign spectral features to various reactants. The possibility of controlling the composition and structure of reduced graphene oxide (rGO) is discussed.

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1. Introduction

Since 2004, when Novoselov and Geim published their ground-breaking work about the preparation and characterization of graphene [1], great interest in this material developed. Soon there was the demand for new synthesis methods, because using this method, which was described by Novoselov and Geim, was only suitable for research. Starting with this motivation, graphene oxide (GO) was proposed to be a possible precursor to graphene [2]. GO is now known since more than 150 years as graphitic acid [3]. Today there is renewed interest in it because of many possible applications published in the past years [4,5].

GO and rGO (reduced graphene oxide) are of interest because they cover other qualities than graphene, synthesized by chemical vapour deposition. A key aspect is the easy functionalization of the oxygen containing groups. Investigating these materials is a continuing concern within sensor [6–9] and electronic applications [10].

The exact structure of GO is still under discussion, but the Lerf-Klinowski model is generally accepted [11]. It states that the single sheets in graphite are decorated with the most different oxygen

containing groups, mostly alcohols, epoxides and at the sheet edges carboxylic acid groups. The structure is non-ordered and a recent electrochemical study showed that the final GO structure depends even on the synthesis method [12].

The oxygen containing groups affect the properties of this material. They decrease the hydrophobicity of the sheets and make a dispersion of GO and the exfoliation to single nanosheets in water (depending on the pH) [13] and other solvents possible [14]. As soon as the single sheets are separated from each other, the main challenge is to reduce GO to a graphene-like structure. The electrochemical reduction [15] is favoured, because, structural defects can be healed [4] and aggressive reductants can be avoided. In the literature, it was published as green method [16]. It is easy to perform, especially when metal surfaces shall be coated, and is thus proposed for many possible applications.

Therefore, the reduction mechanism and the structure of the final product are of great interest. There is minor literature on the reduction of GO in organic solvents [17], which shows that the C=O, O–H and C=C bonds play an important role in the reduction of GO. Water is an important medium for the reduction and is used in numerous proposed applications. Investigations in H₂O [18] showed that several oxygen containing groups are reduced in a small potential range. Due to the diverse chemical structure of GO it has to be assumed that the electrochemical reduction takes place in several steps.

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This study allowed to clarify the multistep mechanism of the electrochemical GO reduction by an *in-situ* attenuated total reflection FTIR (*in-situ* ATR-FTIR) spectroscopy investigation. The formation and degeneration of oxygen containing groups during the cathodic reduction of GO is described. A comparison of IR results of aqueous and D₂O solutions served to elucidate the mechanism. In this context, the multivariate curve resolution - alternating least squares (MCR-ALS) was a powerful tool for interpreting perturbed spectroscopic data [19–21]. The resulting spectra of this multicomponent system are overlapping. Moreover, there are minor differences between the concentration profiles in respect to the electrochemical potential. Therefore, conventional peak fitting methods fail in contrast to applied MCR-ALS.

2. Experimental

2.1. Electrode design on the ATR-prism and *in-situ* spectroelectrochemical procedures

GO was obtained commercially (Graphene Laboratories Inc.). The flake size was between 0.5 μm and 5 μm . The proportion of single layer GO sheets was >80%.

The *in-situ* electrochemical ATR cell was designed with a 3D construction software and produced by a 3D printer (Ultimaker B. V.; model Ultimaker²) on the basis of acrylonitrile butadiene styrene.

A conventional potentiostated three electrode setup (potentiostat: Electrochemical Workstation, CH-Instruments 760C) with a platinum wire as counter electrode and an Ag/AgCl/3 M KCl electrode as reference electrode (0.21 V vs. SHE) was used. All potentials are given vs. the standard hydrogen electrode (SHE), if not otherwise stated.

To obtain adequate sensitivity for the GO reduction, a special pattern was prepared on the ZnSe ATR crystal. It was coated with a Au grid, which was connected to the potentiostat as working electrode (compare Fig. 6). The uncoated area served as the ATR detection region. Only on these uncoated ZnSe surfaces electrochemically induced (from the Au grid electrode surface) infrared-active changes can be registered.

Physical vapour deposition was performed to prepare this grid. Two 3mm broad Au stripes were deposited by gold evaporation on a 45° ATR prism as electrical contacts for a finer grid electrode grid. This was generated by Au evaporation through a mask of thin copper wire rungs.

To improve the wetting behaviour of GO suspensions during spin coating, a self-assembled monolayer of 4-mercaptophenole was prepared on this gold grid. The prism was cleaned with EtOH p. A. abs. A vessel for the self-assembling was cleaned with a 3:1 conc. H₂SO₄/30% H₂O₂ solution, water, EtOH p.A. abs. 9.8mg 4-mercaptophenole were dissolved in 50 ml EtOH p.A. abs. The prism was immersed for 24 h, cleaned with EtOH, and dried under Ar.

GO was deposited by spin coating on the ATR prism. 5 ml of a commercial 6.2 mg/ml suspension were mixed with 25 ml EtOH p. A. abs. An adapter for the spin coater made of acrylonitrile butadiene styrene was designed and produced by a 3D printer to coat the ZnSe prism directly (Ultimaker B.V., model Ultimaker²). The spin coating routine consisted of four equivalent steps of coating and drying for 20 min at 600 rpm.

The thus-prepared crystal was mounted in the spectroelectrochemical cell (Fig. 1). An Ar flushed 1 M Na₂SO₄ solution (in H₂O or D₂O) was filled into it. FTIR spectra were recorded during cycling voltammetry. The sampling time of one spectrum was 100 s, corresponding to 122 single scan spectra and a resolution of 4 cm⁻¹. According to the scan rate of 0.5 mV/s, this corresponded to a potential scan variation of 50 mV per spectrum.

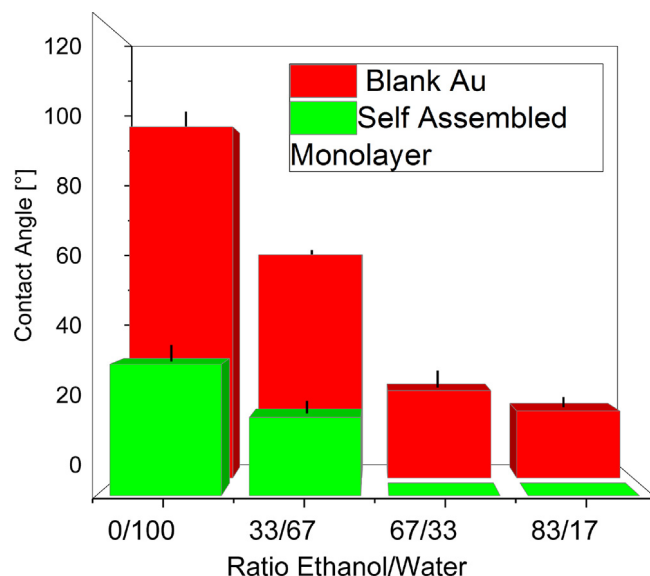


Fig. 1. Contact angle vs. water/ethanol ratio with and without mercaptophenole SAM.

2.2. Determination of the graphene oxide coating thickness

A spin coating routine was calibrated on Au coated glass to determine the thickness of the spin coated GO samples. A defined groove in the GO coating was generated by femtosecond pulse laser ablation. 45 GO samples with three different thicknesses were processed using a Ti:Sapphire Chirped Pulse Oscillator (modified Femtosource XL, Femtolasers Produktions GmbH) delivering pulses with a full width half maximum duration of 60 fs at a central wavelength of 800 nm with a repetition rate of 11 MHz. Pulses were picked with a Pockels cell at a rate of 5 kHz. The beam was guided into a research microscope (Zeiss AxioImager.M1 equipped with a Zeiss EC Plan-NEOFLUAR 10x/0.3 objective). The focus position was determined before each experiment with a custom system [22]. The applied fluence was 0.11 Jcm⁻², which is below the threshold fluence of the gold. Thus, the underlying Au substrate stayed intact.

The as prepared samples were scanned with a scanning force microscope (NTEGRA Aura EC; NT-MDT) in contact mode at constant force (CSG10 tip, NT-MDT). The spring constant of the cantilever was 0.4 N/m. The z-noise of the SFM scanner was 0.1 nm. Measurements were done in ambient conditions (25°C, 35% relative humidity).

2.3. Peak fit routine

The spectra were fitted by a peak fit routine based on a commercial software (OPUS, Bruker Corporation) using a

Table 1
Parameters for the peak fit routine

Position [cm ⁻¹]	Width [cm ⁻¹]	Position [cm ⁻¹]	Width [cm ⁻¹]
1097.4	63.1	1641.9	57.5
1205.8	55.0	2366.4	135.7
1327.1	35.4	2479.7	150.3
1366.9	32.3	2611.4	144.4
1425.6	33.8	2782.1	28.5
1458.9	31.7	2863.7	40.4
1500.9	31.6	2925.5	41.6
1552.1	37.1		

Levenberg-Marquardt algorithm. The applied parameters are presented in Table 1.

2.4. Multivariate curve resolution - alternating least squares

The basic model of this method is the idea that the resulting spectra can be obtained by a matrix multiplication of a matrix containing the pure spectra and a matrix containing the concentration profiles:

$$D = C \cdot S^T + E \quad (1)$$

Equation (1) shows this relation, where D ($M \times N$) is the experimental spectra matrix obtained by the experiment, M is the number of spectra and N is the number of data points per spectrum. C ($M \times F$) is the matrix of the concentration profiles, where F is the number of pure components. S^T ($F \times N$) is the transposed spectra matrix of the pure components and E is the residuals matrix [20,21].

The goal of this method is to obtain the C and S^T from D by optimization. To do this, F must be estimated before. This can be done by various methods: singular value decomposition, evolving factor analysis, or principal component analysis. Initial estimates - like nonnegativity or unimodality - give adequate starting conditions for the iterative ALS (alternating least squares) optimization of the two matrices.

The MCR-ALS analysis was performed in MATLAB R2015a (MathWorks) with a tool optimized for this environment [21].

Before starting the MCR-ALS routine, the number of components was determined by singular value decomposition. The initial spectra estimation was performed by an algorithm based on the simple iterative self-modelling approach (SIMPLISMA).

For the MCR-ALS optimization the following constraints were applied. The spectra and the concentration profiles were assumed to be non-negative. The concentration profiles were also set to be unimodal and the sum of all concentrations was set to 1 at a specific point in time. This means that for each consumed reactant a product evolves or that all participating compounds are represented in the spectra, which is the case for the studied system.

3. Results and Discussion

3.1. Preparation of the graphene oxide coatings

We optimized the surface of the ATR-prism for spin coating. To produce homogeneous GO coatings, the GO-suspension must wet the hydrophobic gold surface. An addition of ethanol to the water suspensions improved the wetting behaviour (Fig. 1; red bars).

An increasing volume ratio of ethanol/water yielded a not complete wetting. An addition of 4-mercaptophenole SAM led to a complete wetting already at a volume ratio of ethanol/water of 67/33 (Fig. 2; green bars). Therefore, 4-mercaptophenole SAMs were applied to all Au surfaces throughout this study.

3.2. Thickness of the graphene oxide coatings

Fig. 2 shows a laser-generated groove in a GO coating. The thickness of the coatings was determined to be ca. 3 nm per coating step, which corresponds to three GO single layers (assuming one GO sheet with a 1.1 nm thickness [16]).

The results of three different thicknesses are shown in Fig. 3. The linear regression shows a slope of 3.0 ± 0.6 nm, which means that each coating step led to 3 nm. Four coating steps were applied on the samples for the *in-situ* measurements. 12 nm thick layers used for the investigations corresponded to 11–12 GO sheets.

3.3. Cyclic Voltammetry

The spectroelectrochemical reduction of GO in D_2O and H_2O solutions on the Au grid shows two reduction waves at -0.5 V and

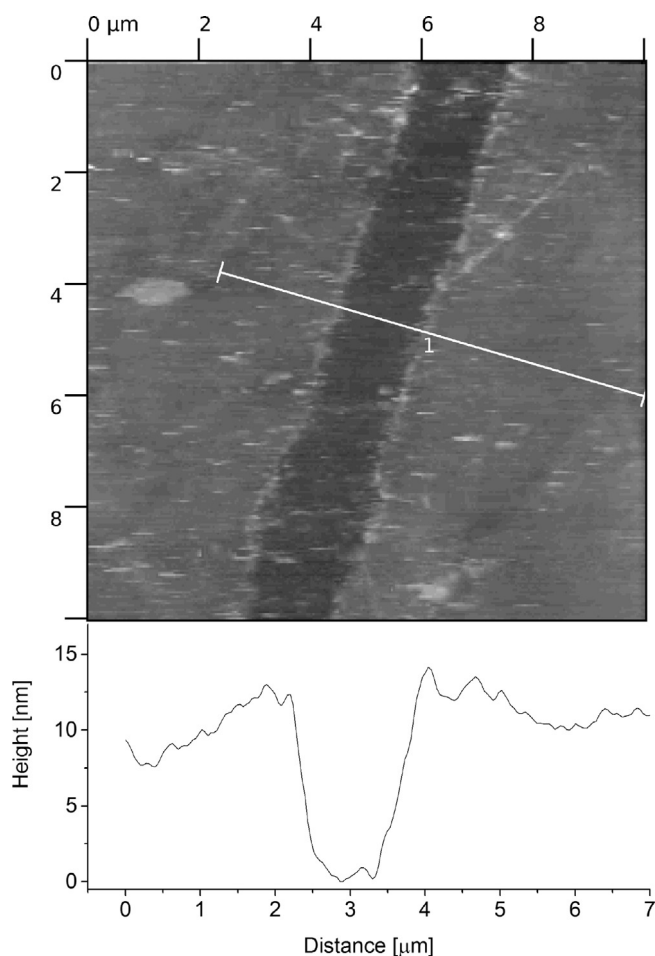


Fig. 2. Exemplary AFM image of a graphene oxide coated sample, prepared with 3 coating steps in the spincoater. The line was ablated with a femtosecond laser. The depth of the line is appr. 10 nm corresponding to 9–10 graphene oxide sheets.

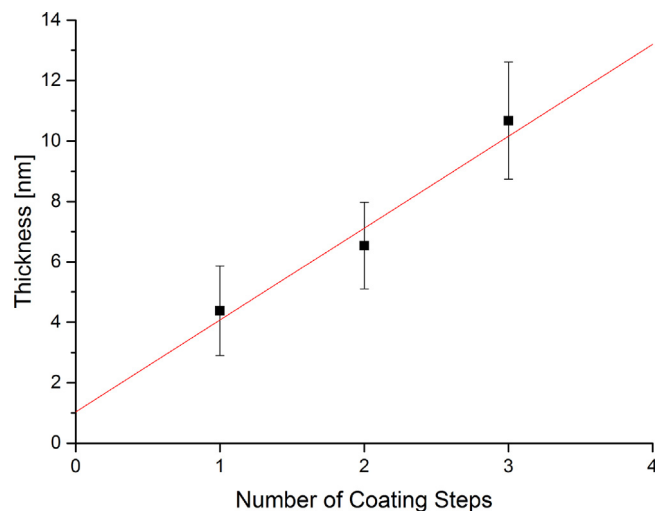


Fig. 3. Calibration of the spin coating routine. Average thicknesses of graphene oxide coatings with 1, 2 and 3 coating steps.

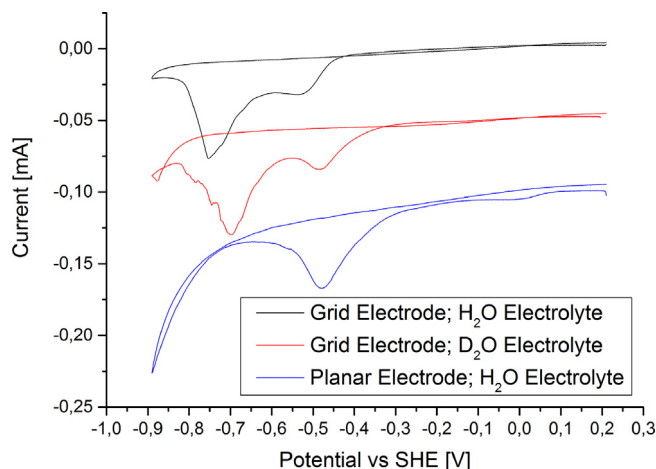


Fig. 4. Cyclic Voltammetry of the graphene oxide coating in the measurement cell on the Au grid in H_2O (black), Au grid in D_2O (red), and on planar Au in H_2O (blue).

–0.7 V during the first reduction potential scan (Fig. 4 black and red curves).

The two overpotentials for the GO reduction suggest two different rGO regions, one directly on the Au electrode surfaces (Fig. 5), and the other between the grid fingers directly on the insulating ZnSe surface. The rGO with the lower reduction overpotential (–0.5 V, Au surface) can be interpreted as those rGO regions directly grown on the Au grid fingers exhibiting low series resistance. It was shown that GO, synthesized by permanganate oxidants, can be oxidized electrochemically after its electrochemical reduction [12].

On the ZnSe surface the rGO showed a distorted reduction peak and an increased reduction overpotential because the laterally growing film exhibits an increased internal series resistance. Due to the shape of this reduction peak at –0.7 V it can be assumed that the GO reduction proceeds in a multistep mechanism.

A comparison of this findings with an analogous experiment on planar Au (Fig. 4 blue curve) affirms this theory. Here, only the reduction peak at lower overpotentials (i.e. the GO directly on the Au grid) appears. The other reduction peak, which comes from the grid structure, vanishes. These results are consistent with measurements from the literature [18], where the reduction of GO was observed in this potential region.

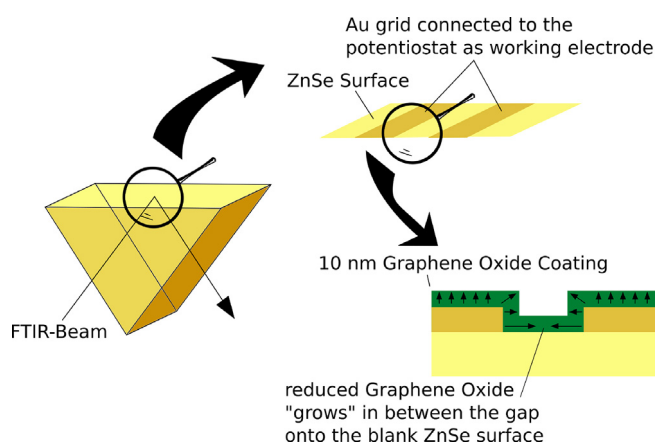


Fig. 5. Detection surface of the ATR crystal. The graphene oxide coating lies over a Au grid, where it is reduced electrochemically. Reduced graphene oxide grows into the gaps between the grid fingers, where it can be detected by ATR-FTIR.

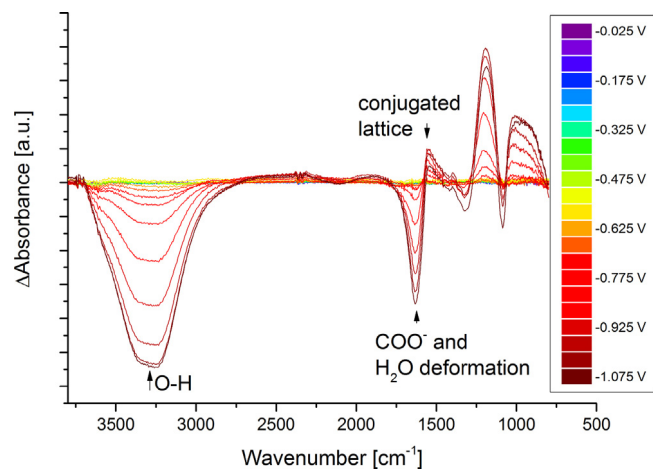


Fig. 6. *In-situ* FTIR reduction of graphene oxide in H_2O . The conjugated lattice can be assigned to reduced graphene oxide, the COO^- stretch vibration to graphene oxide.

This special electrode structure on the ATR crystal shows important consequences for the ATR-FTIR measurements: Au-surface-rGO is shaded by the electrode fingers and is therefore excluded from any spectroscopic recording. On the ZnSe surface, on the other hand, rGO grows laterally between the Au fingers directly on the ATR crystal, and therefore can be directly detected by the spectrometer (Fig. 5). Thus, the peak at –0.7 V is interpreted and discussed in this work.

This assumption can be supported by the FTIR evaluation, where the reduction at –0.7 V results in significant changes in the spectra (whereas the one at –0.5 V does not). Therefore, it confirms that it takes place directly on the ZnSe surface.

3.4. *In-situ* ATR-FTIR measurements in H_2O

In the *In-situ* ATR-FTIR spectra of the reduction of GO in H_2O positive bands represent the evolution, and negative bands the consumption of a respective interfacial species (Fig. 6).

The negative band at 1640 cm^{-1} represents the COO^- bonds of the GO, and thus the reduction to rGO. rGO is also observable based on the evolution of a conjugated lattice represented by the band at 1552 cm^{-1} .

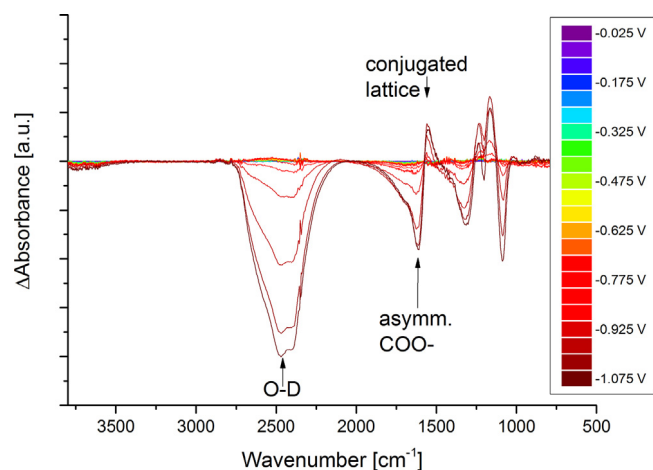


Fig. 7. *In-situ* FTIR reduction of graphene oxide in H_2O . The conjugated lattice can be assigned to reduced graphene oxide, the COO^- stretch vibration to graphene oxide.

Table 2
Shift of the vibration bands in water and heavy water [24]

Indication	Water	Deuterated Water
$\nu_{as,s}$	3000 – 3500 cm^{-1}	2200 – 2700 cm^{-1}
δ	1500 – 1800 cm^{-1}	1100 – 1400 cm^{-1}

A strong negative band in the O–H stretch vibration region between 3000 cm^{-1} and 3500 cm^{-1} can be correlated with the O–H reduction on GO. However, solvent water also absorbs in this region. It should be considered that the extent of the evanescent IR-field depends on the different refractive indices of interfacial species such as GO and rGO [23]. Therefore the measured absorption of the water bands changes. The GO and rGO coating is not affected, because it is much thinner than the extent of the evanescent field. This concerns O–H between 3000 cm^{-1} and 3500 cm^{-1} as well as the region of the COO^- bonds at 1640 cm^{-1} , where the deformation vibration of water is also expected. Therefore, the quantitative interpretation in the solvent H_2O is difficult.

3.5. In-situ ATR-FTIR measurements in D_2O

The spectra of the *in-situ* measurements in D_2O show a clearer view (Fig. 7).

The heavier deuterium is in excess compared to hydrogen. Therefore, any protic groups contain only deuterium because of dissociative exchange of hydrogen. Its concentration can be neglected. Thus, the bands of the deuterated groups are shifted to lower wavenumbers (see Table 2). Consequently, all bands, which were not shifted due to the use of D_2O , can be identified as aprotic groups.

The water deformation vibration shifted from 1640 cm^{-1} to lower wavenumbers. Thus, it does not overlap with spectral feature of GO in this region. A strong band at appr. 1600 cm^{-1} can now be assigned to carboxylate groups.

In previous literature [17,16] a C=O vibration was observed at wavenumbers around 1750 cm^{-1} . Our spectra show a very small feature in this region. The band at 1600 cm^{-1} is more prominent. We performed our experiments under aqueous conditions. Therefore, the observed bands of the carboxylate group are the symmetric and asymmetric COO^- stretch vibrations [25,26] - instead of the C=O stretch vibration.

These findings presume that carboxylate groups exist in their deprotonated form. It was reported [13] that the zeta potential of

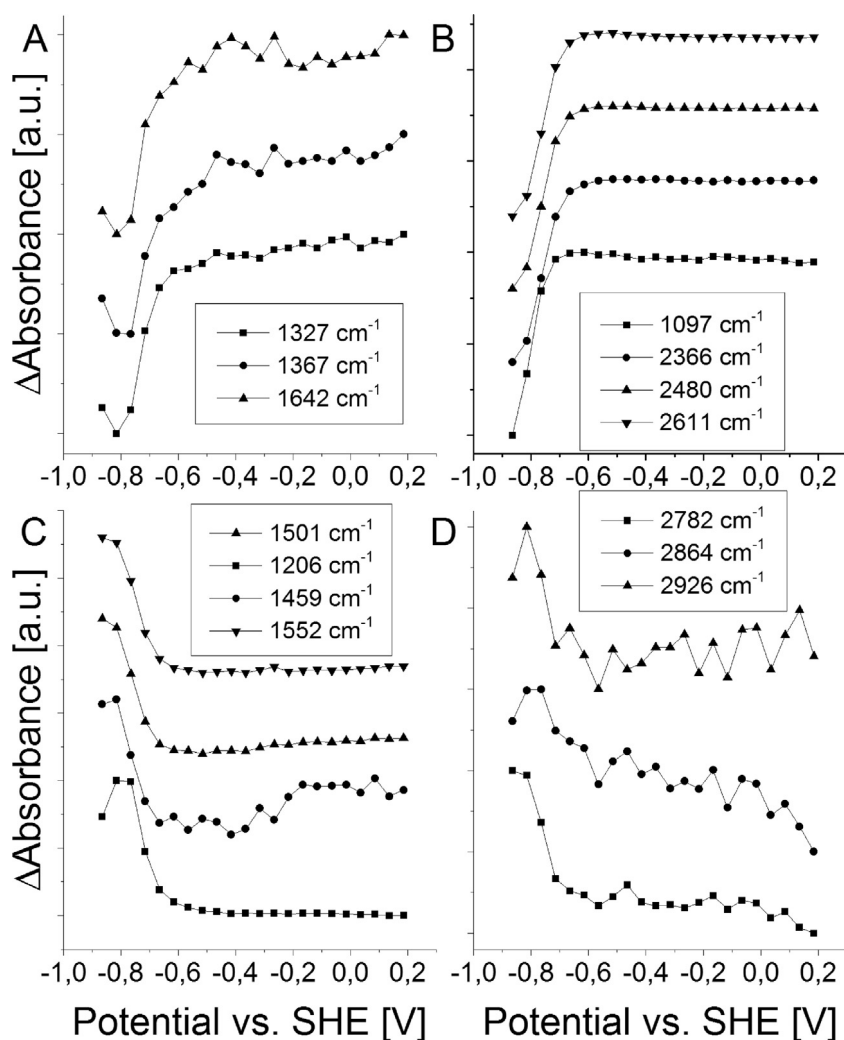


Fig. 8. Peak fit results of the spectroelectrochemical reduction of graphene oxide in D_2O ; A: Reduction of graphene oxide. B: Reduction of α -reduced graphene oxide. C: Formation of reduced graphene oxide. D: Reduced graphene oxide shows the formation of aliphatic C–H bonds.

GO sheets is appr. -35 mV for pH 4 and higher. Below this pH it rises up to -15 mV. Carboxylate groups are deprotonated above pH 4 due to the correlation of the zeta potential and the protonation. Na_2SO_4 solutions (pH 6–7) were used in the present study. Even though they were unbuffered, a cathodic polarization could result only in an increased local pH due to possible reduction reactions of oxygen and/or water. Therefore, carboxylic acid groups must be deprotonated in this system.

This is supported by the two pK_a values of carboxylate groups on GO of 4.4 and 6.6 [25]. Although it can be argued, that the acid groups with $\text{pK}_a = 6.6$ are just partially dissociated, FTIR spectra showed that at pH 5 and above no $\text{C}=\text{O}$ vibration was visible at 1730 cm^{-1} in accordance with our work.

The bands were fitted via a peak fit routine. The bands can be grouped into two sets. The first is synchronously reduced at approximately -0.67 V (Fig. 8 A). For simplicity, the first set is called α -rGO, and the second set, at the more cathodic potential of -0.70 V, is named β -rGO (Fig. 8 B and 8 C). The results of Fig. 8 can be compared with the calculated clean spectra in Fig. 9 B.

The bands at 1327 cm^{-1} and 1367 cm^{-1} (Fig. 8 A) belong to different oxygen containing groups with $\text{C}-\text{O}$ bonds, most probably to epoxides (asymmetric stretching, [27]). The reduction of these groups proceeds synchronously at a less cathodic potential than those of the second set shown in Fig. 8 B.

The band at 1642 cm^{-1} in the first set can be assigned to the asymmetric COO^- stretch vibration (Fig. 8 A). The potential behaviour of this band corresponds to the observed band in the spectrum at 1600 cm^{-1} . The higher wavenumber is due to the unsatisfying peak separation of the peak fit routine and may not be interpreted quantitatively. Clearer results were gained through MCR-ALS, reported in section 3.6.

The most prominent bands in Fig. 8 B are the ones at 2366 cm^{-1} , 2480 cm^{-1} and 2611 cm^{-1} . They can be assigned to the $\text{O}-\text{D}$ stretching vibrations of different oxygen containing groups in GO, mainly alcohols. However, the solvent absorbs in this region as well. A clear relationship to GO was shown by the Multivariate Curve Resolution (see section 3.6). Analogous bands at higher wavenumbers were observed in the measurements in H_2O not shown here. The band at 1097 cm^{-1} shows a clear correlation to the second band set, the formation of β -rGO and the reduction of α -rGO. It refers to the $\text{C}-\text{O}$ vibration of the alcoholic groups or epoxide groups. Both were reported in literature in this region [12,16,18].

Fig. 8 C shows increasing bands of the generated rGO. Figs. 8 A and 8 B suggest a stepwise reduction, which cannot be detected from Fig. 8 C. A MCR-ALS analysis (see section 3.6) takes the synchronicity of the signals into account and supports this finding. The cyclic voltammogram (Fig. 4) shows that the cathodic wave between -0.67 V and -0.8 V consists of at least two hardly resolvable reduction waves.

The bands at 1552 cm^{-1} , 1501 cm^{-1} and 1459 cm^{-1} can be assigned to aromatic groups which start growing at a potential negative of -0.70 V. 1552 cm^{-1} represents skeletal vibrations of the conjugated lattice, i.e. sp^2 -carbon bonding which leads to an increase of conductivity [28,29].

The bands at 1501 cm^{-1} and 1459 cm^{-1} refer to substituted aromatic regions. However, the band at 1206 cm^{-1} increases already at a potential of -0.67 V where the bands in Fig. 8 B were reduced.

The band at 1206 cm^{-1} may be interpreted to represent a $\text{C}-\text{O}$ group generated by the reduction of a COO^- group. The slight decrease of the absorption at the cathodic reverse potential confirms this, because this COO^- group is most probably reduced to an alcoholic group, which then is further reduced at more cathodic potentials. A MCR-ALS evaluation supports this interpretation (Section 3.6).

The bands at 2782 cm^{-1} , 2864 cm^{-1} , and 2926 cm^{-1} represent $\text{C}-\text{H}$ stretching vibrations in aliphatic regions (Fig. 8 D) [24]. Hydrogen bonded to aliphatic regions is not exchanged in D_2O . These bands became detectable because the normally overlapping $\text{O}-\text{D}$ vibrations are shifted to lower wavenumbers in contrast to $\text{O}-\text{H}$ stretching vibrations. This observation suggests that the electrochemical reduction of GO containing defects such as five- and seven membered rings can result in the formation of $\text{C}-\text{H}$ bonds in aliphatic regions.

3.6. Multivariate curve resolution - alternating least squares evaluation

Based on the above described peak-fit method and a principle component analysis [21] one can assume the involvement of three species. This is the conventional way for treating such data, as described in this paper. However, the central issue is not how certain bands in the spectrum behave, but how the reactants and products, i.e. GO, α -rGO, and β -rGO, change.

Their concentration-potential dependence is represented in Fig. 9 A.

It can be seen that the reduction occurs in two steps. At first the COO^- groups of GO (black curve) are reduced to the product α -rGO (red curve). In a second step this is reduced to β -rGO (blue curve). The corresponding spectral development takes place in the same

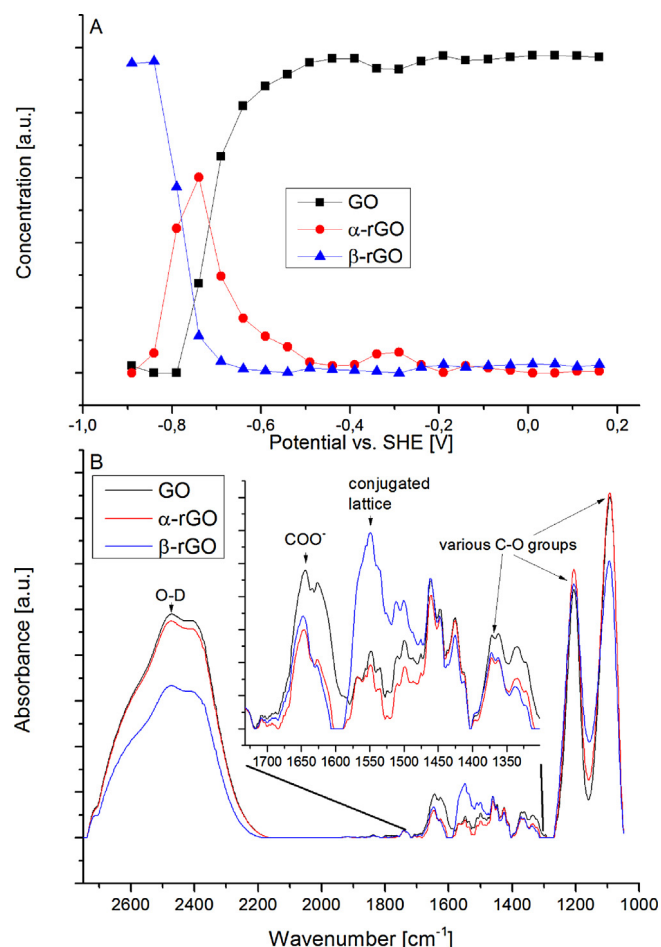


Fig. 9. Results of Multivariate Curve Resolution. A: Concentration courses. B: Clean spectra.

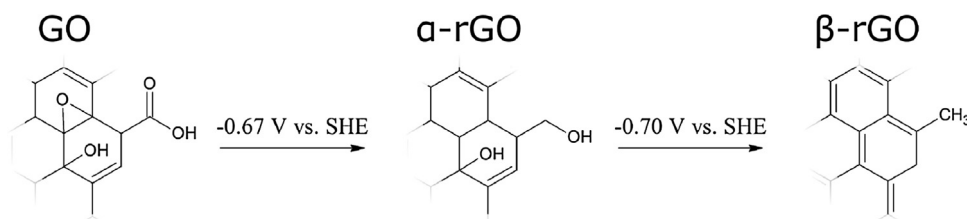


Fig. 10. Postulated 2-step reaction mechanism of the electrochemical reduction of graphene oxide.

potential region as the reduction waves at -0.75 V to rGO on the ZnSe-surface (Fig. 4).

The above described peak fit routine delivers the trend of various bands. The results of MCR-ALS do not only provide the concentration profiles of the reactants, but also the IR-spectra of GO, α -rGO, and β -rGO (Fig. 9 B).

The spectra are in accordance with the already discussed results and give even more insight into the electrochemical reduction mechanism of GO. The first step of this mechanism is characterized by the decrement of carboxylate groups. This feature can be seen between 1600 cm^{-1} and 1700 cm^{-1} . As mentioned above, the position and the peak shape emphasise that the carboxylate groups exist in their deprotonated form.

Below 1400 cm^{-1} the spectra show several features, which were assigned to different groups containing C–O bonds. The reduction of COO^- groups in GO must result in the generation of C–O bonds in α -rGO. This can be seen in a slight increase of the band at appr. 1200 cm^{-1} . During the reduction of α -rGO to β -rGO it decreases again.

Of course C–O bonds are present in many different chemical groups, which differ also in their electrochemical behaviour. The Lerf-Klinowski model [11] suggests the presence of alcoholic groups, carboxylic acid groups, and epoxides, which all contain C–O bonds. Probably the real structure of GO is even more complicated than that. Therefore some C–O bonds are reduced in the first reduction wave from GO to α -rGO (between 1300 cm^{-1} and 1400 cm^{-1}) and others are reduced in the second reduction wave from α -rGO to β -rGO (below 1300 cm^{-1}).

The reduction wave from α -rGO to β -rGO is mainly characterized by two features: the reduction of alcoholic groups and the formation of a π -conjugated lattice. The decrease of the bands of the O–D stretch vibration between 2200 cm^{-1} and 2700 cm^{-1} show the reduction of the alcoholic groups. Since they decrease together with the C–O band at appr. 1100 cm^{-1} , this latter band can be assigned to a C–OD vibration. The formation of the π -conjugated lattice is observed at the spectral region around 1550 cm^{-1} .

4. Conclusion

The electrochemical reduction of GO was investigated in aqueous media. The cyclic voltammogram showed two reduction waves, one referring to the gold grid surface, and the second correlated to the regions directly on the ZnSe crystal between the grid fingers. Only this surface region directly on the ZnSe could be monitored by *in-situ* FTIR. The evaluation of the spectroelectrochemical data by a peak fit routine and Multivariate Curve Resolution-Alternating least squares showed that the reduction takes place in two steps (Fig. 10). At first, carboxylate groups are reduced to C–O bonds. The resulting product was called α -rGO which itself was further reduced to β -rGO. In this second step C–O bonds and O–D bonds were reduced indicating the reduction of alcoholic groups.

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